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**REPORT AMXTH-TE-CR-84308**

**SURFACE SAMPLING TECHNIQUES USING  
ULTRAVIOLET ILLUMINATION**

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Ivan Simon  
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**ARTHUR D. LITTLE, INC.  
CAMBRIDGE, MA 02140**

NOVEMBER 1984

FINAL REPORT  
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*prepared for*

United States Army Toxic and Hazardous Materials Agency  
Aberdeen Proving Ground, Maryland 21010-5401

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## SUMMARY

Under Contract No. DAAK11-83-C-0062 to the U.S. Army Toxic and Hazardous Materials Agency, Arthur D. Little, Inc. has investigated methods for in-situ detection of explosives on building material surfaces when such surfaces are illuminated by short-wave ultraviolet (UV) radiation. The explosives (analytes) investigated were 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrophenylmethylnitramine (Tetryl), cyclotrimethylene trinitramine (RDX), pentaerythritol tetranitrate (PETN), and diphenylamine (DPA). Surfaces used in the laboratory studies were transite, concrete (patio blocks), wood (pine), metal (stainless steel), brick (common red), and glazed brick (drain pipe). Two potential detection systems were evaluated experimentally: ultraviolet reflection photography and thermal image radiometry.

In laboratory tests the photographic detection method was found to detect low levels--10-20 micrograms/square centimeter ( $\mu\text{g}/\text{cm}^2$ )--of all of the analytes except PETN on concrete, transite and stainless steel. None of the analytes could be detected by this method on wood and brick, nor was PETN detected photographically at low levels on any of the surfaces.

The thermal image radiometric method of detection was unsuccessful in detecting low or even moderately high levels of the analytes on any of the surfaces.

The photographic system comprises a 254 nanometer (nm) illuminator providing on the order of 260 microwatts/square centimeter ( $\mu\text{W}/\text{cm}^2$ ), a Hasselblad 500 C/M camera with a Zeiss 105 millimeter (mm) UV Sonnar lens in combination with a Corion narrow bandpass interference filter (251-257 nm). Tri-X film in the 120 roll format and Polaroid Type 667 pack film are useful recording media. At present, the photographic system is limited to areas on the order of six to seven square feet for each photograph.

In field evaluations of the photographic system, indications of possible surface contamination were noted for certain areas at the Joliet Army Ammunition Plant (JAAP). The photography at the Holston Army Ammunition Plant (HAAP) was inconclusive based mainly on the fact that the area had been recleaned as well as the effect of infrared reflection recorded on the film.

An alternate detection scheme for UV reflection has been considered, namely use of a UV sensitive video tube. Such a system appears feasible with the use of illuminators more powerful than the ones used to date.

## 1. INTRODUCTION

As part of its mission, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) has responsibility for assessment and control of toxic and hazardous materials contamination on Army properties, including associated technology development Department of Defense (DOD)-wide. In carrying out this part of its mission, USATHAMA needs to be able to detect off-post migration of toxic and hazardous materials and the possible contamination by such materials of real estate properties identified for release or other use. Those properties include various DOD installations which have been the site of chemical/explosives manufacturing operations over the past 45 years. Before such installations can be released as surplus government property, USATHAMA must determine whether their subsequent use should be unrestricted. To assist in that determination, USATHAMA must be able to identify any areas contaminated with explosives which could present a safety hazard during subsequent use.

Military explosives and propellants production involves several steps<sup>1</sup>:

- manufacture or purchase of ingredients;
- combination of ingredients into blends, grains, or formulations;
- loading of bombs, etc. with the blends or formulations; and
- final assembly and pack-out.

Each of these steps may result in accidental contamination of the installation environment. For example, the manufacturing step includes pumping of liquids, stirring of slurries, heating and cooling of process streams, filtrations, evaporations, dryings, bagging and boxing, and other usual chemical manufacturing operations. During each of these operations workplace surfaces may be contaminated by spillage or dusting of solids or by spillage of process liquids or liquid wastes. While stringent precautions are taken to control and remove any such contamination, traces of explosives, intermediates, or explosives by-products may be left on floors, walls, ceilings, equipment and in partitions, drains, or other ordinarily inaccessible areas. These areas may be made of concrete, brick, transite, wood, and/or metal building materials.

At a typical Army Ammunition Plant (AAP), the number of such potentially contaminated surfaces is large, and may be widely distributed in many buildings over a substantial area. The development of sampling protocols for identifying all such areas is clearly a formidable task requiring, at a minimum, procedures that are capable of detecting small amounts of explosives while permitting the rapid screening of large areas. Furthermore, a sampling

protocol could reasonably be required to satisfy a number of additional requirements including, for example, the following:

- it should be specific for the analyte(s) of interest;
- it should not result in an irreversible chemical reaction which could make the analyte unavailable for subsequent treatment or additional testing;
- its use should not present an unusual hazard to the operator; and
- it should not result in a net increase in the amount of contamination present in and on the surface tested and should not in any other way affect the suitability of that surface for any projected future use.

Under a previous Contract (No. DAAK 11-81-C-0014)<sup>2</sup> to USATHAMA, Arthur D. Little, Inc., investigated available techniques for detection and determination of explosives on common building material surfaces. Among the findings of that investigation was the conclusion that all of the then available methods failed to satisfy one or more of the requirements listed above. Therefore, under the same contract, Arthur D. Little, Inc., proceeded with the development of several new methods. A method for qualitative determination based on detection of charge-transfer complexes formed between an explosive and a visualization reagent applied to the surface was evaluated in the field at two Army Ammunition Plants. A method for quantitative determination based on solvent extraction of samples followed by high pressure liquid chromatographic analysis was evaluated using samples prepared in the laboratory. These methods represented a significant advance over available methods; however, they allowed examination of only relatively small areas at one time.

Under the same contract, Arthur D. Little, Inc., identified new concepts which would permit real-time or near real-time imaging of larger areas and thereby address the principal disadvantage of the qualitative charge-transfer complex and quantitative solvent extraction methods. Those concepts were based on the fact that the materials of interest--TNT, 2,4-DNT, 2,6-DNT, RDX, PETN, tetryl and DPA--have strong absorption bands in the ultraviolet (UV). UV radiation directed at a surface on which these analytes are present may be transmitted, reflected, or absorbed. If the UV radiation is matched to the absorption characteristics of the analyte, some portion of that radiation will be absorbed.

Absorption of UV by the analytes will necessarily be accompanied at the same time by a decrease in the UV reflectance. The analytes might appear as dark areas against a light background when viewed in the UV. The detector for this purpose could consist simply of black and white film in a camera equipped with a lens transmitting the UV and with a filter to transmit only the wavelength of interest. Absorption of UV by an analyte will also produce a small rise in temperature of the material and thermal imaging technology might be used to

sense this increase in temperature, provided that diffusion of the heat into the underlying surface does not proceed too rapidly.

These concepts were verified in laboratory experiments involving several analyte-surface combinations. Demonstration of the power of the techniques was limited due to the lack of data on the UV absorption of substrates and, in the UV photography, by the lack of adequate imaging equipment. Areas of further study were identified which would address those problems and lead to a verified, field-usable system.

This report describes the results of work done under Contract No. DAAK-11-83-C-0062 to develop further ultraviolet photography and thermal image radiometry as methods for screening surfaces for indications of explosives. This methodology was recognized to lack specificity from the analytes since any material having the same UV absorbance at the illuminating wave lengths would produce results similar to the explosives. However, the premise was that the major contamination at an AAP would be the explosive material that was handled there and positive results would be indications of such contamination. The identification of the sampling protocol best suited to analyte-surface combinations and field conditions was the goal of the program. Prototypes for the photographic and thermal imaging sampling protocols were to be developed through laboratory experiments and extended to field tests as applicable. In laboratory experiments, the protocols were to be applied in determining the limits of detection for the analyte/surface combinations.

The development and evaluation of the sampling protocols required investigation of the detection instrumentation (UV camera system and thermal image radiometer), the ultraviolet illumination source, and accessories such as optical filters.

In addition to the experimental and test program of this contract, ultraviolet video technology was to be assessed in theory for feasibility in detection of explosives on building surfaces.

The Sampling Protocols Technical Report and the Analysis Methods Technical Report that were submitted earlier in the program are again submitted in this report as Appendix I and Appendix II, respectively.

## 2. DISCUSSION

### 2.1 Ultraviolet Spectra

The UV photography and the thermal imaging radiometry detection methods rely on enhanced ultraviolet absorptions by the analytes over those expected for the substrates. The essential difference between the two methods is that the reflectance method anticipates that the enhanced absorbance by the analyte will result in a reduced reflectance, whereas the thermal emittance method requires that enhanced absorbance result in a localized heating of the residue on the substrate. The heating in turn must result in an enhanced thermal emission from the residue over that which would normally be exhibited by the substrate itself. As discussed in the previous report<sup>2</sup> the essence of the methods proposed for surveying munitions plants for the presence of residual explosive materials is based on the concept that the ultraviolet reflective/absorptive properties of those materials are different from the underlying substrates.

Although there is much spectral data in the literature concerning the analytes of interest, such data were obtained with solutions. Because absorption bands are known to be affected by solvents and, more importantly, because the survey methods to be studied involved solid explosives, it was necessary to measure directly the reflectance of the analytes in the solid state. In addition, since the literature data on solid construction materials were sparse and/or nonexistent, it was necessary to measure their reflectances.

The total reflectance has two components: specular and diffuse. The specular reflectance is the mirror-like component, in which the angle of reflection equals the angle of incidence. Diffuse reflectance represents the component in which the reflected rays are equally likely to leave the surface at any angle. For an "ideal" rough surface, the intensity of such diffuse reflectance is proportional to the cosine of the angle of reflection. For actual irregularly rough surfaces, this proportional relationship is not necessarily quantitative; the non-directional component of reflection is thus referred to as "quasi-diffuse" reflectance. When the surface roughness occurs on a scale that is large compared to the wavelength of radiation from the source, it is expected that much of the incident energy will be reflected in a quasi-diffuse manner.

Using a Beckman DK-2A spectrophotometer, the total reflectance of all of the analytes and substrates discussed in this report were measured from 220 to 800 nanometers (nm). The analytes were applied as solutions in organic solvents to a silica gel thin layer chromatographic sheet, and the measurements made after the solvents had evaporated. The silica gel sheet was chosen for a substrate because it is highly reflective over the wavelengths examined, readily available, clean, non-reactive, flat, smooth, wettable and thin, thereby minimizing the opportunity for loss of the analyte by penetration into the surface. The results are shown in Figures 1 and 2 which include the

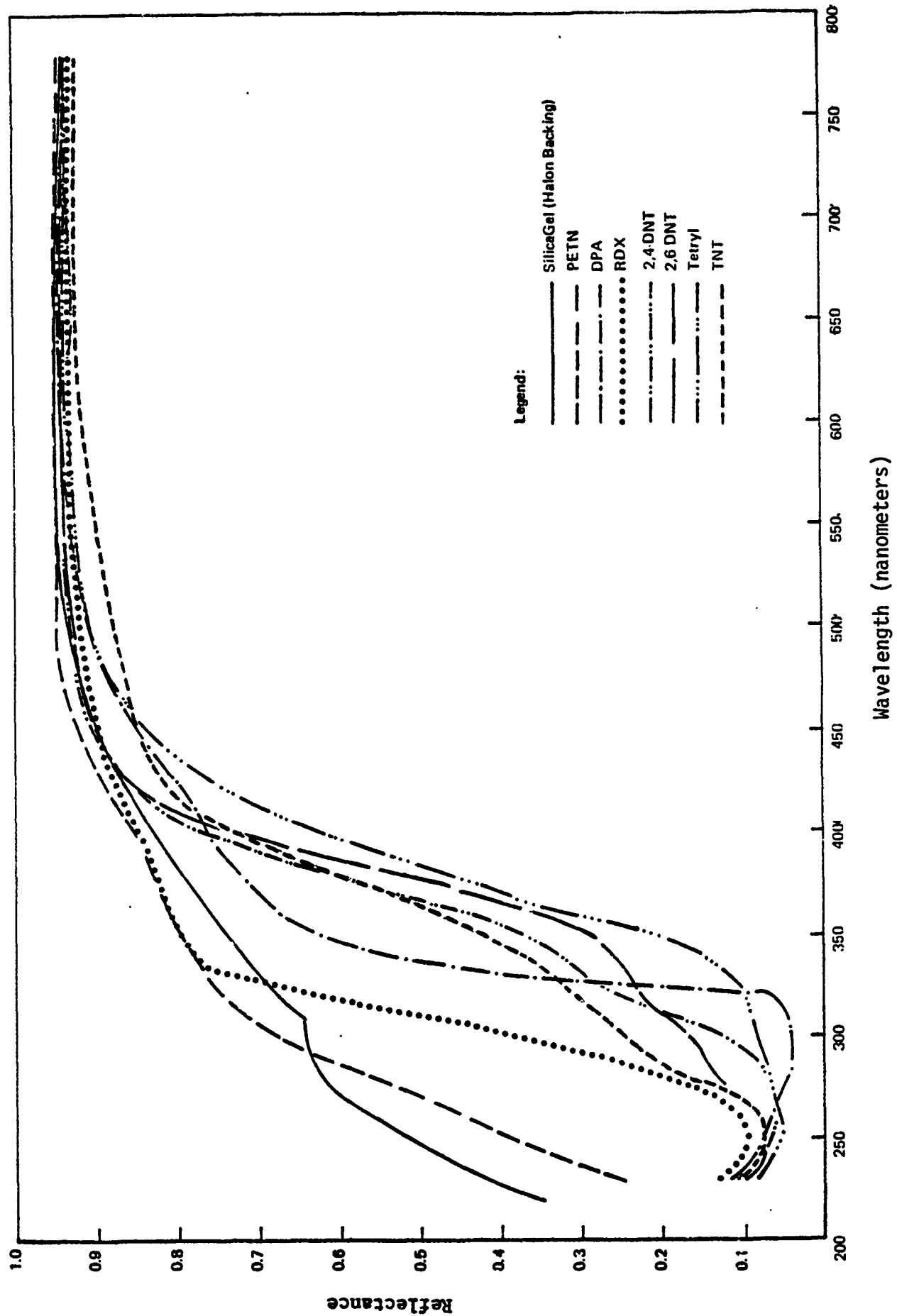


FIGURE 1 TOTAL REFLECTANCE OF ANALYTES

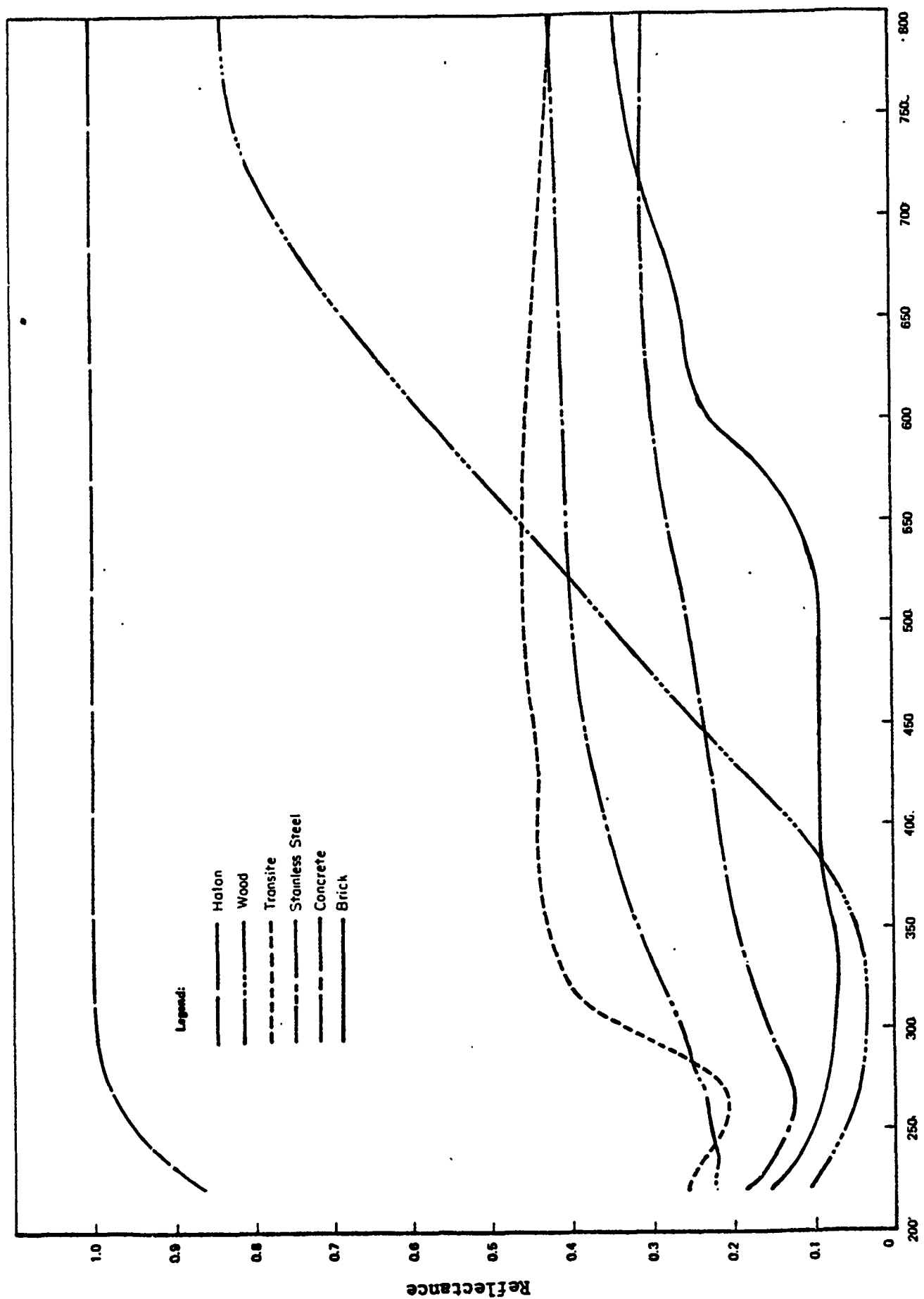


FIGURE 2 TOTAL REFLECTANCE OF SUBSTRATES

spectrum of the silica gel in Figure 1 and the spectrum of Halon in Figure 2 to serve as a standard for reflectance.

The maximum absorption (i.e., minimum reflectance) of the analytes TNT, 2,4-DNT, 2,6-DNT, RDX and tetryl is at or near 250 nm. That of DPA is near 300 nm, while PETN has its maximum absorption at some wavelength less than 220 nm. The latter finding is in agreement with literature data presented in the previously referenced report.

As can be seen in Figure 2, the darkest substrate in the short wave (<300 nm) ultraviolet region is wood (pine) with the transite and stainless steel having the highest reflectances. Most of the substrates shown have minima in the 260 to 340 nm region and their reflectances begin to increase again at the shortest wavelengths measured.

In order to assess the relative importance of specular versus diffuse reflectance processes, another experiment was carried out, measuring the diffuse reflectances of the substrates in the ultraviolet region. Within experimental error ( $\pm 0.02$  reflectance units), the results were the same as the total reflectances except for concrete and transite where a small specular component is observed. The experiment, therefore, served to show that specular reflections in this region are only of minor importance and that diffuse/quasi-diffuse reflectance is the dominant process. This is surprising in the case of the metal surface, which was expected to have a substantial specular component, but not for the other, rougher, surfaces. The fact that the diffuse component dominates the total reflectance implies that the detection system will be less critically dependent on the relative positions of the camera and the irradiation source than it would be if specular reflectance were important.

Examination of the strong absorption bands (minimum reflectance) of the various analytes in the 250 nm region would lead to the conclusion that the method would be very successful on any reasonably bright substrate.

Unfortunately, the data from Figure 2 indicated that the substrates are relatively dark in the 250 nm region and therefore the substantive question to be answered was whether there would be sufficient contrast from the strong absorption bands of the analytes when compared to the relatively low reflectance of the various substrates. One would predict that for an illumination source in the 250 nm region the best results would be obtained with the transite and the metal and the poorest results with the wood and the brick. As will be seen later this is precisely what was found.

## 2.2 Ultraviolet Photography

### 2.2.1 Camera System

In experiments performed under the previous contract, a single element fused silica lens of 250 mm focal length was used. For the purposes of the



experiments at that time, the lens was temporarily taped to a shutter with an added iris for controlling the exposure. This lens and shutter assembly was used with a large Bausch and Lomb Model L camera designed for photomicrography in the laboratory. Due to its bulk and weight, the camera was considered entirely unsuited for field work.

A further problem with that original camera and lens was inherent in the simple lens which was not capable of focussing the full spectrum of visible light onto a single focal plane. The image produced with ultraviolet radiation appeared badly out of focus. It was quite clear from those early experiments that a camera and lens suitable for the purposes of this project would have to be a portable, light-weight camera with full shutter and iris functions for controlled exposures. The lens would have to be capable of producing a clear, sharp image for focussing and picture taking in visible light and, at the same time, be capable of producing a like-quality image with UV radiation.

Our investigations of commercial photographic equipment for the present contract indicated that the Hasselblad Model 500 C/M camera in combination with a Zeiss 105 mm UV-Sonnar C lens would meet the requirements of this project. The camera is well recognized as a high quality professional camera with sufficient reliability to be acceptable for use in such demanding applications as the NASA Space programs. It is small and relatively light in weight (approximately 1.4 Kg). Moreover, besides the standard roll film format (120 size), an accessory is available which enables the camera to be used with a variety of the Polaroid instant films.

The 105 mm UV Sonnar f/4.3 is a special purpose lens made by Zeiss of West Germany especially for ultraviolet photography. The lens consists of fluorite and quartz elements with excellent transmission in the UV spectral range and chromatic correction in the UV as well as the visible spectral range. The spectral range of this lens is from 215 nm through 700 nm. An image focussed in visible light will be in sharp focus through the UV also. The UV Sonnar lens is normally supplied in a mount, complete with shutter and iris, for the Hasselblad camera. Other Zeiss lenses capable of UV transmission are intended for application in projection equipment and would not be readily adapted to photography.

The Hasselblad 500 camera and Zeiss UV Sonnar lens were acquired and used throughout the experimental work on this project and are shown in Figure 3 together with two filters (one mounted in the holder and one on the table) and the universal filter holder.

As stated previously, the Hasselblad camera can be used either with 120 film (negative) or with Polaroid pack film (3½ x 4½ print size). Kodak Tri-X Pan Professional 120 film was the film of choice based on its ASA rating of 320 and the fact that multiple contact prints of good contrast could be produced and, if necessary, enlargements with only slightly lesser contrast as well. Of the available Polaroid products, only print-type film (e.g., Type 667

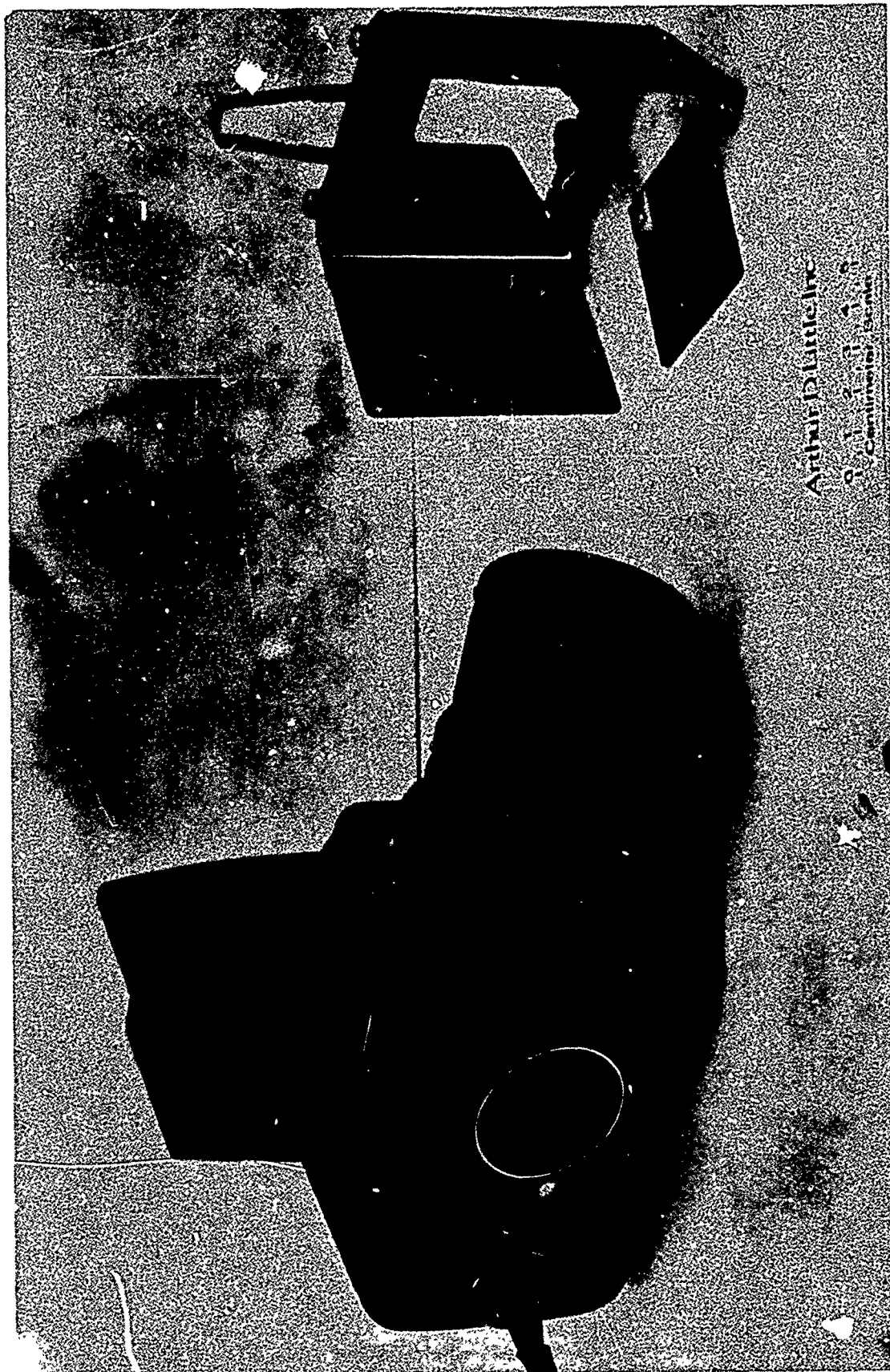


Figure 3. Camera and Accessories

coaterless film with an ASA rating of 3000) would provide adequate speed. This film was considered to be of lesser quality than the Tri-X because of its more grainy rendition of scenes and its lack of ready reproduction of multiple prints, especially enlargements. For this reason, the Polaroid 667 alternative was excluded from the laboratory evaluation and the first field test at Holston AAP. After that first field experience, however, it was decided that it would be useful to carry a Polaroid camera on the second trip, to Joliet AAP, in order to obtain real-time photographic documentation of the sites involved. As an adjunct to this documentation function, the Polaroid camera was also field tested using 667 film and UV illumination to confirm the expected performance of this film versus Tri-X. It was thought possible that the poorer quality image might, nevertheless, provide some useful real-time information on highly contaminated areas. Use of the Polaroid 667 film in UV photography required a modification to the film holder adapter in that a glass insert between the camera and the film had to be removed to allow transmission of the short wave UV to the film.

Since the illumination system would be a source of additional spectral lines other than 254 nm (cf. Section 2.2.2), filters were considered necessary accessories for the camera system. From a comparison of available filters tested in the laboratory, a 2 mm thick UG-5 filter (Schott Glassworks, Mainz, West Germany) was considered suitable. This filter was found to transmit 70% of the UV radiation from 250 nm to 385 nm then rapidly fall to almost zero transmission at 410 nm through 650 nm. In additional laboratory experiments, this filter did prove successful in discrimination of many analytes on concrete, transite, and stainless steel. It was only during the field evaluation at the Holston Army Ammunition Plant (HAAP) that its transmittance above 650 nm was realized to present some problems. Sunlight radiation in the long wave end of the visible spectrum, when it was a factor in the area of interest, produced regions of light and dark (shadows) on the film. Although most UV photography would be restricted to indoor work without the 650 nm and above irradiance, some outdoor areas would definitely necessitate better filtration at the camera lens.

Reconsideration of the requisite filtration led to the testing of a 251-257 nm narrow-band pass filter (Corion Corporation, Holliston, Mass.) This filter transmits only about 10% of irradiance at 254 nm and is totally blocked at other wavelengths. The use of this filter required much longer exposure times for the photography of both laboratory samples and areas of interest in the field sites.

#### 2.2.2 Illumination System

From consideration of the spectral reflectances of the analytes (Figure 1), it was concluded that a wavelength in the vicinity of 250 nm would provide the best illumination for any detection system. Three types of UV sources are suitable for such an illumination, namely low pressure mercury arcs, high pressure mercury arcs, and excimer lasers. Criteria for selecting among these

sources included: maximum irradiance intensity at 254 nm; minimum irradiance at other, undesirable, wavelengths; size and weight (transportable in the field by no more than two persons); and power requirements (120V AC preferred).

Low pressure mercury arc lamps are extremely efficient emitters of radiation throughout the entire line spectrum of mercury but most of the radiation output (~84%) is in the 254 nm spectral line. These lamps are commercially used for germicidal purposes and as such are available in the types and sizes equivalent to tubular fluorescent lamps. They are operated from standard 120V alternating current (AC) lines using conventional ballast fixtures and are available in ratings from 4 to 30 watts with corresponding UV outputs from 0.6 to 8.3 watts. The prices of standard, single-lamp units are moderate--in the range of \$100 to \$200.

High pressure mercury arc lamps have a useful emission of UV in the required spectral range (the 254 nm Hg line, pressure broadened and self-reversed). However, they also emit a number of other mercury spectral lines in the visible and near infrared ranges. This radiation is undesirable and must be filtered out and rejected as heat, which makes the operation rather inefficient. High pressure mercury arc sources could produce the required level of irradiance and their cost would be a fraction of that for equivalent excimer laser sources. However, the need for effective optical filtering and cooling plus a possible explosion hazard involved in their start-up and operation led to rejecting their use in the present work.

Excimer lasers, in particular the KrF laser emitting at 248 nm, tend to be bulky, heavy and expensive (~\$40,000 to \$100,000). They generate a narrowly collimated beam of monochromatic radiation in single or repetitive pulses of a duration of a few nanoseconds. These characteristics, together with the high-voltage pulsing and the need for periodic recharging with toxic gas led to rejecting the excimer laser for the present purpose.

The approximate irradiance of the analytes to produce a suitable photograph was calculated for an assumed average scene from the expression:

$$W = 4Ef^2 (tRTF)^{-1}$$

where,

E: Exposure of the film in watt sec/cm<sup>2</sup> =  $1 \times 10^{-8}$  Ws/cm<sup>2</sup> (for Kodak Tri-X film to produce an image density of 0.6).

f: f number of the Zeiss Sonnar lens = 4.3.

t: The exposure time in seconds, 1/15 sec taken as an example.

R: The diffuse reflectance = 0.1, taken as an example of most analytes in the wavelength region of interest.

T: The transmittance of the lens = 0.6 at 254 nm.

F: The transmittance of the UV filter = 0.7 as an average.

With such values, the irradiance  $W$  is  $2.64 \times 10^{-4}$  W/cm<sup>2</sup> or 264  $\mu$ W/cm<sup>2</sup>. This value was used as a guide for designing the UV illuminator to be used for evaluation of the UV photography system with the intent to use it also in evaluation of the thermal imaging radiometer system.

Before constructing a UV illumination system, laboratory tests were conducted to compare the performance of three different mercury discharge lamps. One was a high pressure mercury lamp and two were different designs of low pressure lamps, namely a germicidal clear tubular lamp and a Mineralight fixture that consisted of a nine-foot tubular coil as the source and a filter to transmit the 254 nm mercury line. The data presented in Table 1 indicate that of the three lamps, the germicidal lamp and the high pressure arc produce the highest irradiance--66 and 68 microwatts/cm<sup>2</sup>, respectively--in the 254 nm region. The irradiance obtained by using more than one lamp is additive; the use of an array of four germicidal lamps to illuminate a surface, for example, would produce an irradiance on the order of 264  $\mu$ W/cm<sup>2</sup>, thereby satisfying the requirement calculated above.

The data presented in Table 1 also indicate that the germicidal lamp produces much less irradiance at lines other than the 254 nm line than does the high pressure arc. For the present purposes the 254 nm line is the only one of importance. The other lines might produce an undesirable background, particularly with the photographic detection method. The germicidal lamp was therefore selected as the UV irradiation source.

Following these tests we constructed the UV illuminator using four 25 watt lamps and fixtures specified in Table 1 (Note 2) in a form of a rectangular frame 30 x 30 inches in size with a 19 x 19 inch opening. The lamp fixtures included quarter-cylindrical aluminum reflectors which directed the UV radiation toward the sample and, together with the frame, shielded the camera from direct illumination by the light source. The camera was aimed at the scene through the center of the frame. Figure 4 shows the front of the illuminator and Figure 5 illustrates one illuminator-camera configuration.

Table 1. Spectral Irradiance Produced by Mercury Discharge Lamps at 1 Meter Distance ( $\mu\text{W}/\text{cm}^2$ )<sup>1</sup>

<u>Mercury Spectral Lines (nm)</u>	<u>LAMP TYPES</u>		
	<u>Germicidal</u> <sup>2</sup>	<u>Mineralight</u> <sup>3</sup>	<u>High Pressure Arc</u> <sup>4</sup>
254	66	8	68
365	0.026	0	8.1
405	0.13	0.4	4.3
436	0.29	0	6.8
546	0.20	0	7.4
578	0.09	0	6.8

NOTES:

<sup>1</sup>All measurements were made using a Model IL 700-A Radiometer. Measurements at 254 nm were made with a Model SEE-240 detector which is substantially blind to any radiation of a wavelength longer than 350 nm. At such wavelengths, the data were obtained using a monochromator Model IL-587 with a detector SEE-038.

<sup>2</sup>This source was a germicidal mercury discharge tube, Cat. No. G25T8 manufactured by American UV Company of Chatham, NJ (mounted in a fixture Cat. No. UFR-25-H, by the same manufacturer) with a half-round reflector. The self-contained unit operates from the 117 volt AC line at a nominal 25 watt input.

<sup>3</sup>This source is an old laboratory "Mineralight" unit (Model S-61, UV Products, Pasadena, CA) equipped with a visible-blocking glass filter. It operates from 117 volt AC line at ~80 watt input.

<sup>4</sup>This source was a high pressure mercury lamp (Cat. #HB0200/2, Osram) mounted in a lamp housing without a condenser lens and powered by a regulated power supply (System #6106, Oriel Corporation, Stamford, CT) at ~49V and 3.4A DC (~167W).

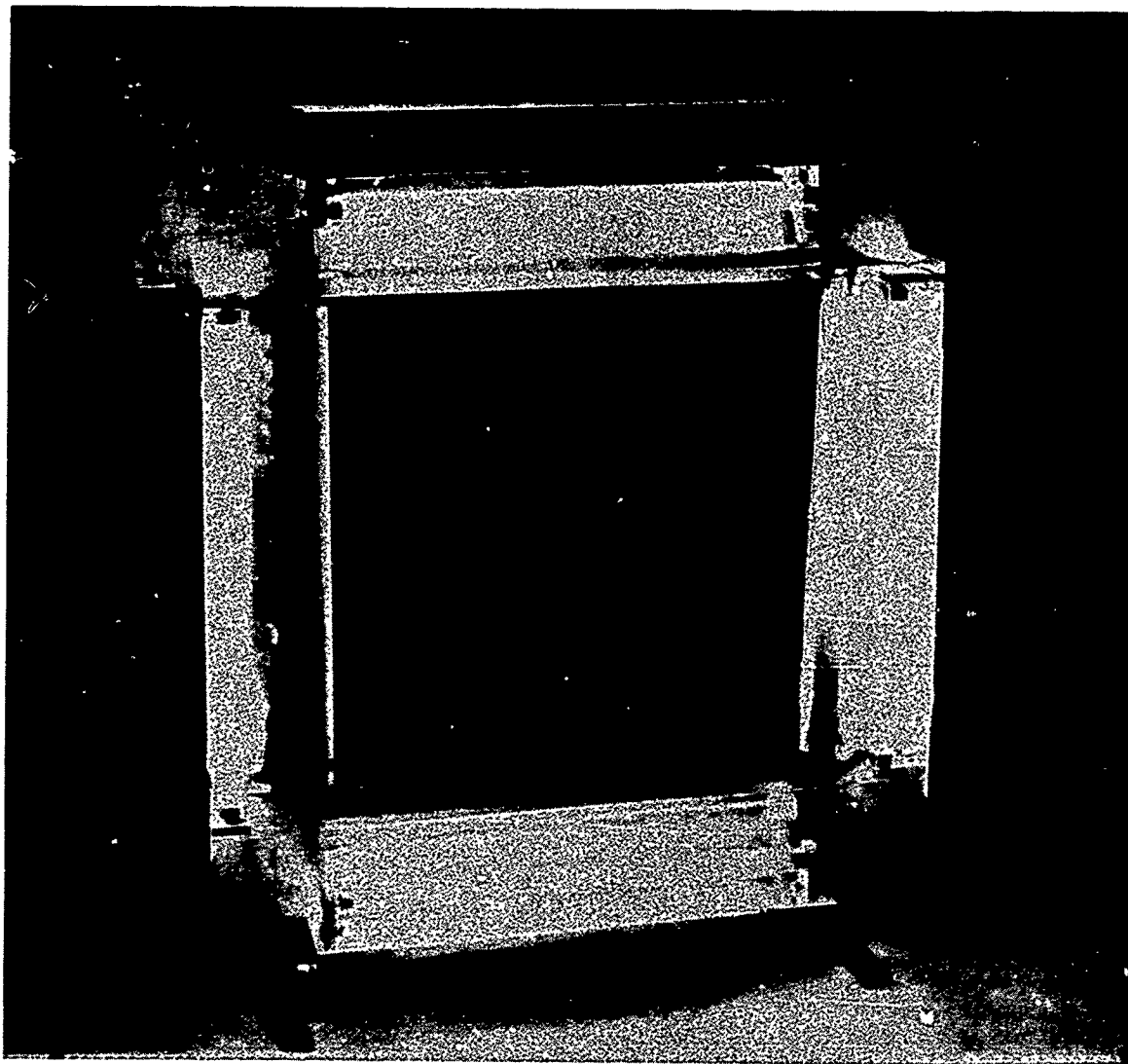


Figure 4. 254 nm Illuminator



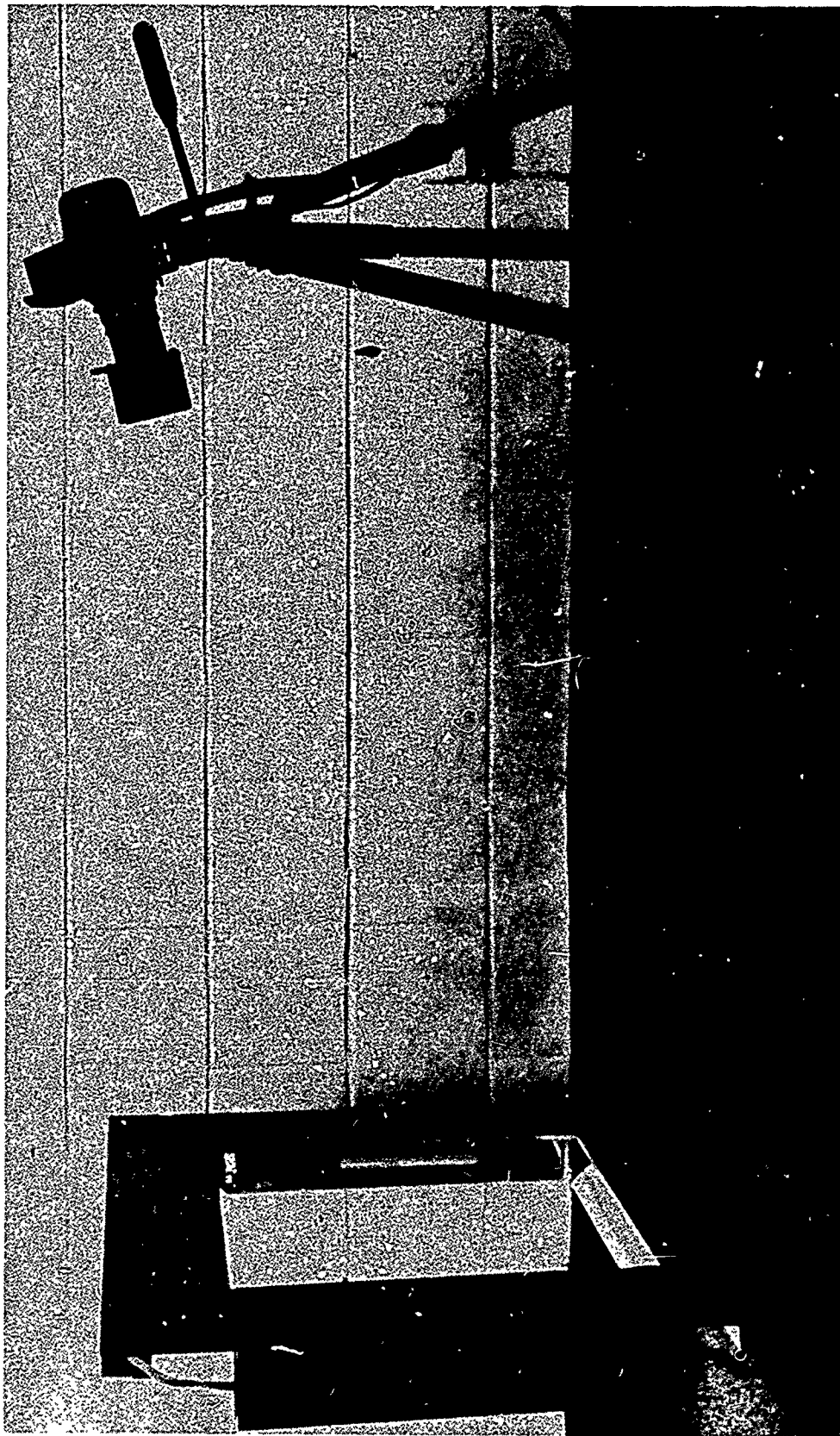


Figure 5. Illuminator - Camera System



The sampling protocol based on the illuminator and camera system became, then, an arrangement generally as follows:

- The illuminator was positioned at a distance of no more than 1 m and usually at 70 cm from the surface to be photographed.
- The camera was positioned near its closest useful distance, 180 cm and essentially central to the opening of the illuminator frame.
- Exposures were made according to the film in use, usually with bracketing of exposures. In the field evaluation with the Tri-X film, 40-second exposures at f/16 produced good contrast and with the Polaroid Type 667 film, slightly less contrast was obtained with 5-second exposure at f/16. The detection limit tests, done under better controlled conditions than in the field (e.g., with more even illumination of vertical surfaces) were better exposed at f/16 for 5 seconds for Tri-X and 1/15 second for the Polaroid film.

### 2.2.3 Experimental Testing for Analytes on Substrates

#### 2.2.3.1 Developmental

Initial testing of both the UV photography and thermal imaging radiometry systems involved the following bulk samples of analytes provided by USATHAMA: TNT, 2,4-DNT, 2,6-DNT, RDX, Tetryl, PETN, and DPA. Stock solutions for testing were prepared quantitatively, by weighing a known quantity of analyte into a volumetric flask and making to volume with solvent. Working solutions were prepared by dilution of the stock. Solutions of RDX and PETN were prepared in acetone while the other analytes were dissolved in acetonitrile. Solutions of the analytes were applied using an automatic pipette in essentially circular patterns on the order of 10 cm<sup>2</sup> in area. (This area was chosen arbitrarily but with the intent to provide sufficient spiked area and surrounding clean surface while minimizing the amount of analyte used). The flow from the pipette was controlled manually to ensure that the rate of spreading and solvent evaporation was sufficient to maintain the analyte within the 10 cm<sup>2</sup> target area. The surfaces to which the analytes were applied were unpainted concrete (patio block), common red brick, glazed drain tile, transite (abestos millboard), wood (pine), and stainless steel. The wood, concrete, brick, and transite were obtained from local building supply houses and selected as new and clean items. The stainless steel used in the experiments consisted of trays from an in-house photography laboratory. Some initial experiments were performed to determine whether surface pretreatment (e.g., use of silicone coating) affected the results. No significant differences between treated and untreated surfaces were observed. Furthermore, it was decided that testing of untreated surfaces, as received, would most closely simulate the situation likely to exist in the field.

On steel, concrete, and transite, the mass of each analyte was varied from 2,000 to 50 µg/10 cm<sup>2</sup>. Thermal imaging radiometry, to be discussed more fully

in Section 2.4, was found unsatisfactory in detecting the analytes when illuminated as for the photographic procedure described in 2.2.2 above. The UV photographic system did detect the analytes down to the detection limits indicated in Table 2. These represent the quantities of analyte that had to be applied to assure that the analyte was actually "seen" on the substrate. The total quantities of analytes used in these experiments are discussed in Appendix II.

Table 2. UV Photographic Detection Limit with Bulk Analyte Samples  
( $\mu\text{g}/10\text{ cm}^2$ )

<u>Analyte</u>	<u>SURFACE</u>		
	<u>Concrete</u>	<u>Transite</u>	<u>Steel</u>
TNT	250	250	250
2,4-D	500	250	250
2,6-D	500	250	250
Tetryl	250	250	250
RDX	250	250	250
PETN	1000	1000	1500*
DPA	500	250	250

\*Evident only at edge of area, perhaps due to crystallization of most of sample at circumference.

In the case of the glazed drain tile, its curved surface produced a direct reflection of the illuminator, a reflection that interfered with photographic detection of analyte. DPA, chosen as a model highly non-reflective analyte, was applied at concentrations up to  $2000\text{ }\mu\text{g}/10\text{ cm}^2$  on the drain tile without overcoming the brightness effect of the source reflection.

In the case of analytes on common brick and on wood, the UV reflection photography did not differentiate the analytes from non-treated surface areas. Up to  $2500\text{ }\mu\text{g}$  of each analyte was applied to wood and up to  $5000\text{ }\mu\text{g}$  of each to brick (common), with no detectable image against background. This was not totally unexpected since the data in Figures 1 and 2 (Section 2.1) indicate wood and brick have reflectance at  $254\text{ nm}$  very similar to the analytes. (Tetryl on wood, in ordinary room lighting, is visible to the eye as a yellow stain at  $250\text{ }\mu\text{g}/10\text{ cm}^2$ ). The lack of a detectable image on the unglazed (common) brick surface may have been compounded by a tendency of the analyte solution to penetrate into the porous substrate. This is a different failure mode from that observed with the glazed tile, where the problem was surface reflection. Attempts to make the procedure work on common brick by sealing the surface with a silicone coating were unsuccessful; no improvement in image detectability was observed.

#### 2.2.3.2 Detection Limits

Because of the results of the laboratory tests of the bulk analytes (Table 2), experiments to determine the detection limit using standard analytical reference materials (SARM) were restricted to stainless steel, concrete, and transite. Additionally, since the thermal imaging radiometry was not successful, the detection limits were investigated only with the UV photographic system. The analytes were initially evaluated with  $200\text{ }\mu\text{g}$  of each in an area

of 10 cm<sup>2</sup>, a concentration selected on the basis of the tests with the bulk materials. Each analyte was tested at that level on concrete, transite, and steel, and except for PETN, all could be distinguished in comparison to the blank. However, the image at the 200 µg/10 cm<sup>2</sup> level was sufficiently weak for most analytes that this level was judged to be the effective detection limit for 2,4-DNT, 2,6-DNT, RDX, and DPA; lowest levels of these analytes were therefore not experimentally tested. Since tetryl and TNT appeared considerably more evident (darker) in initial SARM tests, they were also applied at the 100 µg/10 cm<sup>2</sup> level. The photographic results (contrast) at these levels led to the conclusion that the detection limits were 100 µg/10 cm<sup>2</sup> for TNT and tetryl. Because PETN bulk samples were not readily detected at levels on the order of milligrams/10 cm<sup>2</sup> it was decided not to pursue a detection limit based on UV photography of that analyte. Reference to Figure 1 indicates the reflectance of 254 nm UV by PETN would not appear in much contrast to the substrates.

The Rank Sum Test, as given in the April 1982 Sampling and Chemical Analysis Quality Assurance Program, has been applied with the results shown in Table 3.

Figures 6 through 11 are reproductions of photographs taken during the Rank Sum Tests on the three substrates and include PETN as well as the two concentrations of TNT and of tetryl. (It should be noted that these do not show so much contrast as the original contact prints.)

#### 2.2.3.3 Field Evaluations

Ultraviolet photography was tested in the field to assess utility for scanning large areas for residual contamination by explosives. The two sites, Holston AAP in Tennessee and Joliet AAP in Illinois, were visited in June and August of 1984, respectively. These sites had been used during the prior contract (No. DAAK 11-81-C-0014)<sup>2</sup> and used in the evaluation of the solvent-wick system devised to detect explosives. The 1984 trips were to the same areas visited in 1982 at the two AAP's.

The photography at Holston was not expected to reveal much about contamination since a) the earlier testing indicated a very few areas with contamination, and b) the areas had reportedly been subjected to additional cleansing since the 1982 trip. One significant finding during the Holston site visit was that some areas where direct daylight illumination occurred provided radiation near the infrared end of the visible spectrum that did register photographically. As stated in Section 2.2.1 above, the optical filter in the camera system at that time was a Schott UG-5 which was known to transmit above 650 nm. However, because of its high transmittance of 254 nm radiation, it had been chosen for the photography. Most of the photography did not involve direct daylight illumination and did not show distinctive differences in UV reflectances of various areas used in the evaluation. One tool, a skimmer, appeared to have areas less reflective than the overall surface, indicating the possibility of contamination on it. The lack of general evidence of contamination was consistent with the result of the prior solvent-wick tests

Table 3. Rank Sum Test for Qualitative Certification

Surface - Concrete

<u>Analyte</u>	<u>Level Spiked</u>	<u>Blank Sample Response</u>			<u>Spiked Sample Response</u>			<u>Sum of Mean Ranks for Negative Response</u>	<u>Qualitative * Detection Limit</u>
TNT	100 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	100 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	
2,4-DNT	200 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	200 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	
2,6-DNT	200 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	200 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	
RDX	200 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	200 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	
Tetryl	100 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	100 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	
DPA	200 µg/10 cm <sup>2</sup>	(Rank Assigned)	1	2	3	4	5	6	200 µg/10 cm <sup>2</sup>
		(Mean Rank of Group)	-	-	-	+	+	+	
			2	2	2	5	5	5	

\* Based on examination of contact prints from Tri-X 120 film.

Table 3 (Continued). Rank Sum Test for Qualitative Certification

Surface - Stainless Steel

Analyte	Level Spiked	Blank Sample Response					Spiked Sample Response	Sum of Mean Ranks for Negative Response	Qualitative * Detection Limit
TNT	100 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	100 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		
2,4-DNT	200 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	200 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		
2,6-DNT	200 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	200 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		
RDX	200 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	200 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		
Tetryl	100 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	100 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		
DPA	200 $\mu\text{g}/10\text{ cm}^2$	(Rank Assigned)	1	2	3		4 5 6	6	200 $\mu\text{g}/10\text{ cm}^2$
		(Mean Rank of Group)	-	-	-		+ + +		

\* Based on examination of contact prints from Tri-X 120 film.

Table 3. (Continued). Rank Sum Test for Qualitative Certification

Analyte	Level Spiked	Blank Sample Response		Spiked Sample Response		Sum of Mean Ranks for Negative Response	Qualitative * Detection Limit
		(Rank Assigned)	(Mean Rank of Group)	(Rank Assigned)	(Mean Rank of Group)		
TNT	100 µg/10 cm <sup>2</sup>	1	2	3	4	5	100 µg/10 cm <sup>2</sup>
		-	-	-	+	+	
2,4-DNT	200 µg/10 cm <sup>2</sup>	2	2	2	5	5	200 µg/10 cm <sup>2</sup>
		-	-	-	+	+	
2,6-DNT	200 µg/10 cm <sup>2</sup>	1	2	3	4	5	200 µg/10 cm <sup>2</sup>
		-	-	-	+	+	
RDX	200 µg/10 cm <sup>2</sup>	2	2	2	5	5	200 µg/10 cm <sup>2</sup>
		-	-	-	+	+	
Tetryl	100 µg/10 cm <sup>2</sup>	1	2	3	4	5	100 µg/10 cm <sup>2</sup>
		-	-	-	+	+	
DPA	200 µg/10 cm <sup>2</sup>	2	2	2	5	5	200 µg/10 cm <sup>2</sup>
		-	-	-	+	+	

\* Based on examination of contact prints from Tri-X 120 film.

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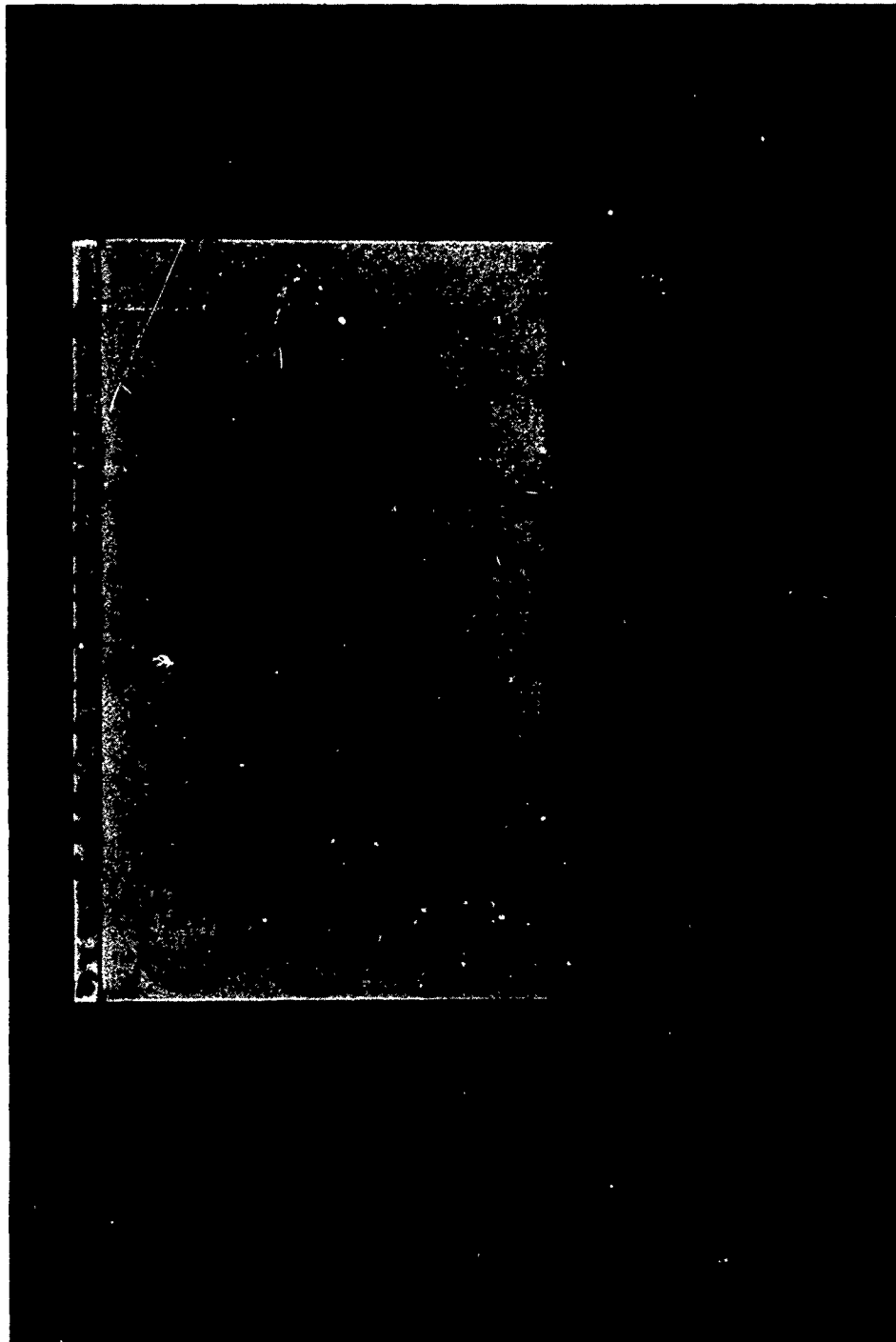


Figure 6. Analytes on Stainless Steel  
DPA; Tetryl; 2,6-DNT; 2,4-DNT; TNT at 200  $\mu\text{g}$  over 10  $\text{cm}^2$   
Blank: acetonitrile = B



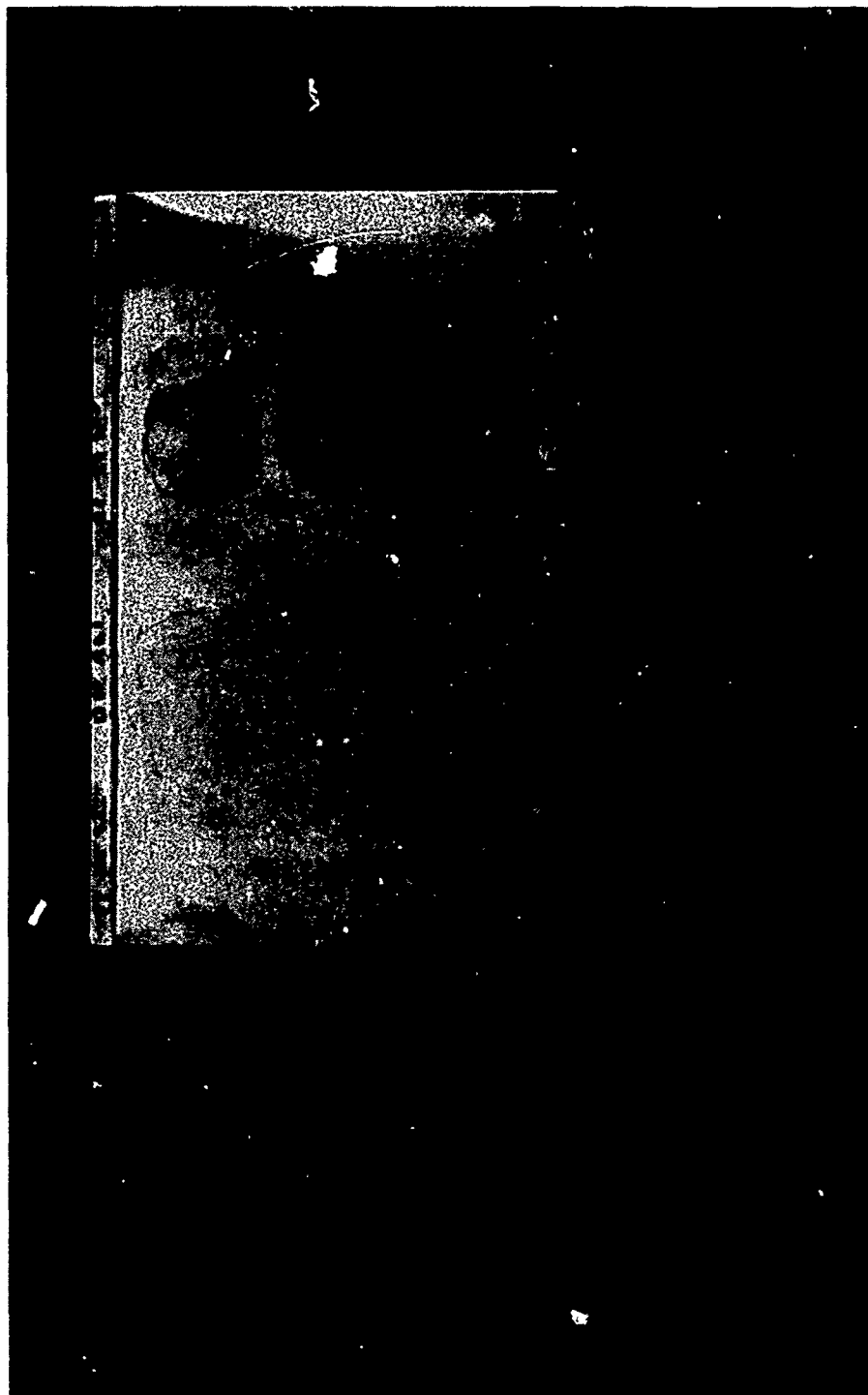


Figure 7. Analytes on Stainless Steel

Blank: acetone = DMK  
PETN and RDX at 200  $\mu\text{g}$  over 10  $\text{cm}^2$

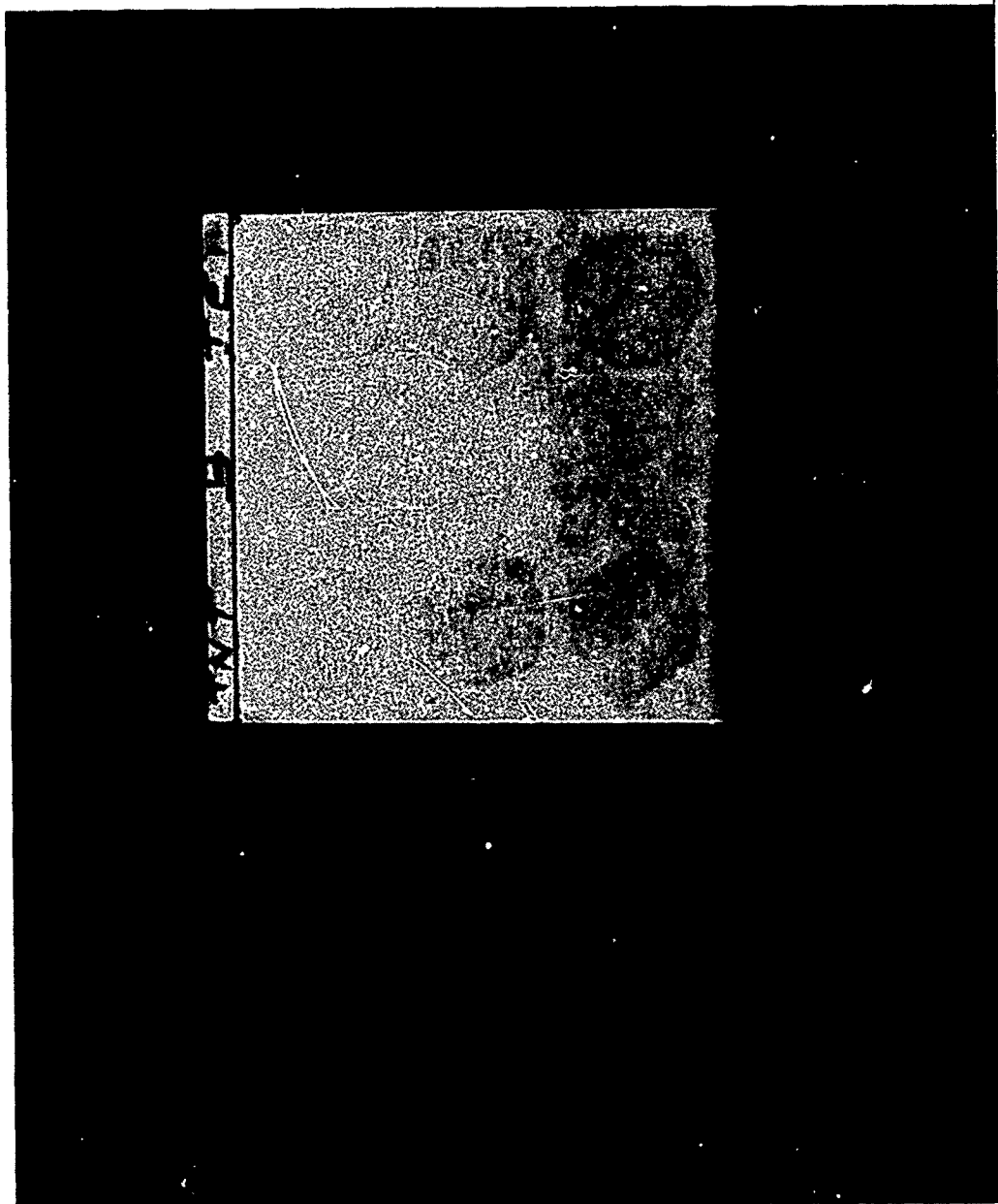


Figure 8. Analytes on Stainless Steel

Blank: acetonitrile (center column)<sub>2</sub>  
TNT and Tetryl at 100  $\mu\text{g}$  over 10  $\text{cm}^2$



Figure 9. Analytes on Transite  
DPA; Tetryl; 2,6-DNT; 2,4-DNT; TNT at 200  $\mu\text{g}$  over 10  $\text{cm}^2$   
Blank: acetonitrile = BLK

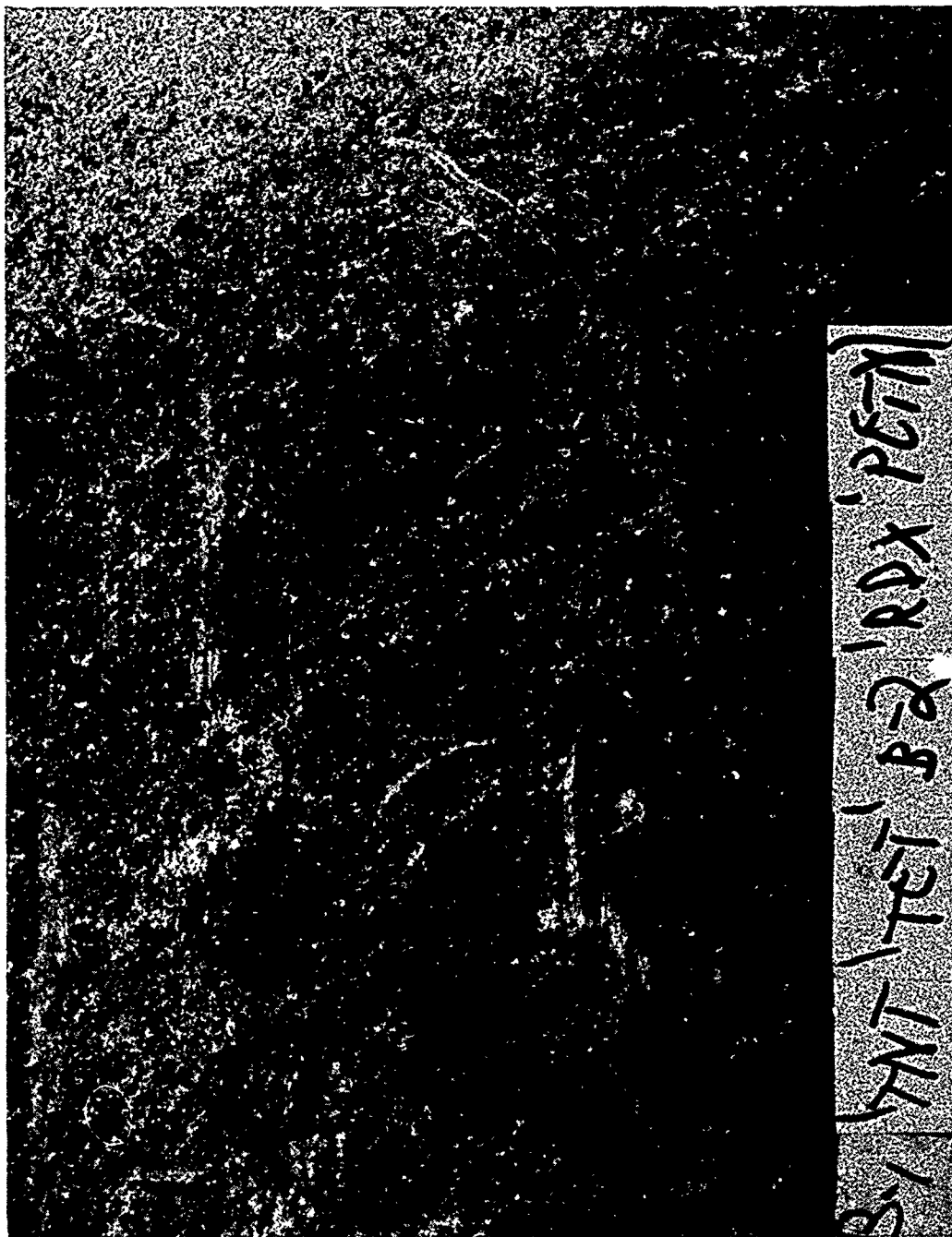


Figure 10. Analytes on Transite

Blank: acetone/nitrile = B-1; TNT and Tetrayl at 100  $\mu\text{g}$  over 10  $\text{cm}^2$ ;  
 Blank: acetone = B-2; RDX and PETN at 200  $\mu\text{g}$  over 10  $\text{cm}^2$

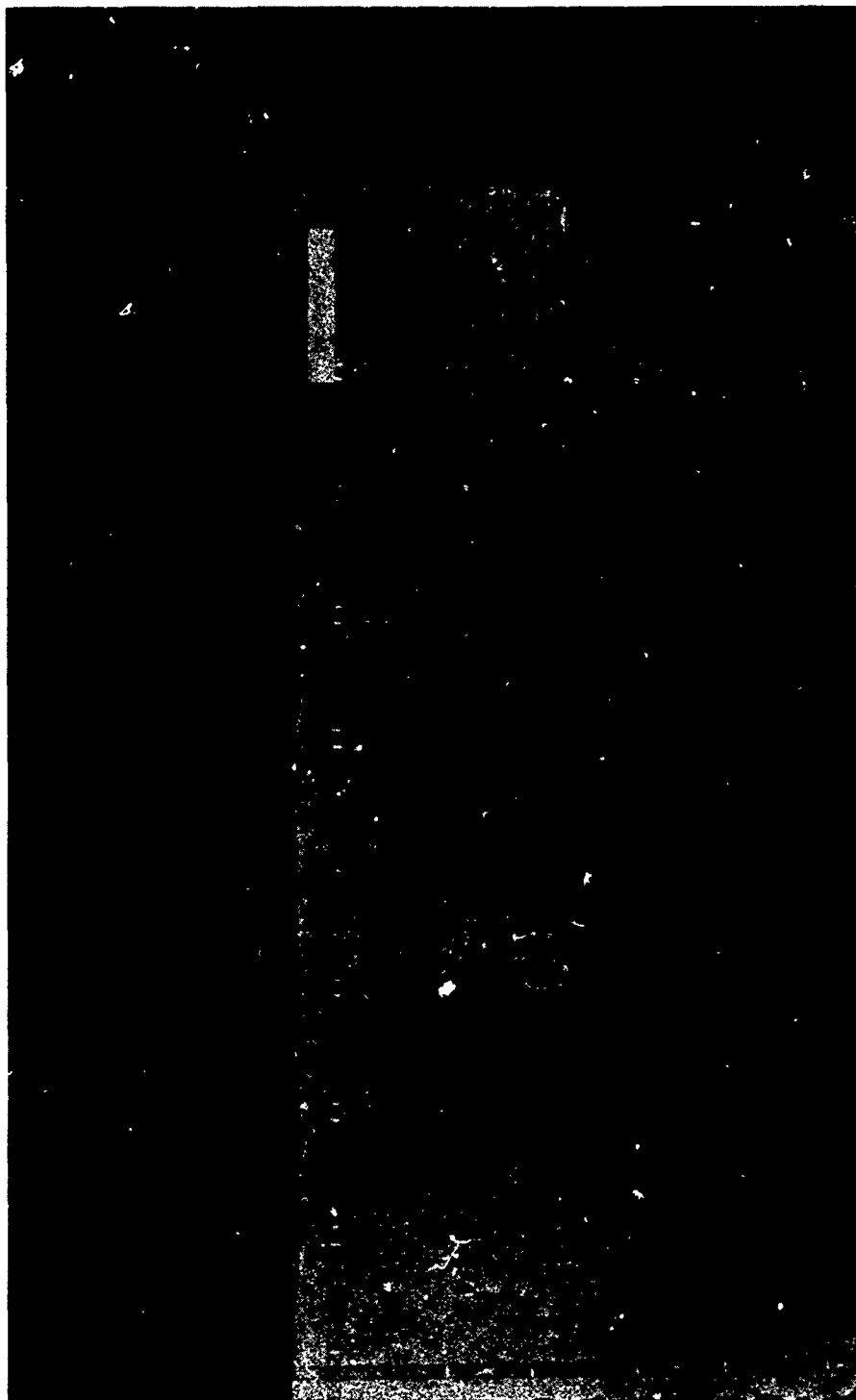


Figure 11. Analytes on Concrete

Order: acetonitrile blank; TNT; 2,4-DNT; 2,6-DNT; Tetryl;  
DPA; RDX; PETN; acetone blank  
TNT and Tetryl at 100  $\mu\text{g}$ ; others at 200  $\mu\text{g}$  over 10  $\text{cm}^2$

and an indication of no false positive results in a well-cleaned area. As a result of this trip to Holston AAP, use of a better filter was investigated, especially for use in direct daylight illumination.

The photography at the Joliet AAP was done with the narrow band pass Corion filter described in Section 2.2.1 and again was done in areas where the solvent-wick system had been evaluated in 1982. Additionally, as time permitted, some solvent-wick tests were carried out during this second trip to Joliet AAP as possible confirmatory evidence of positive or negative photographic results. The solvent-wick procedure is described in Appendix III.

Figures 12 through 14, reproduced from the Tri-X 120 film, are photographs of three locations in which the presence of explosive materials are considered likely by reason of decreased UV reflectance. Figures 12a and 12b are photographs taken in visible and UV illumination, respectively, of an area in Building E-4 on the 2nd floor in Bay 1. This was a TNT melting area and the photographs correspond to the concrete flooring along the wall separating Bay 1 from Bay 2, extending from a line 42 inches from and parallel to the stairway for a distance of 38 inches. The width of the floor area photographed is approximately 30 inches at the top and 20 inches at the lower part of the picture. In Figure 12a taken with visible light, some obvious differences caused by dust can be seen on the surface of the floor patterns of sole prints of shoes and boots. In Figure 12b, some effect of the dust is still apparent. However, both smaller spots and the large less reflective areas extending from the lower left corner of the photo to the overall area in the upper region are considered to indicate potential contamination. Of four solvent-lifts made in the area during the 1984 Joliet AAP site visit, three indicated positive contamination when tested for fluorescence quenching. The fourth lift result was negative and the area tested corresponds to the more reflective region near the lower right corner in the photograph. Since this was a TNT processing area, it must be noted that TNT on concrete takes a reddish visible color even at low concentrations and it is probable that both the spots and general areas of low reflectivity do indicate TNT contamination. The three positive solvent wipe samples all show some visible coloration on the paper substrate. (Arrows numbered 1, 2, and 3 in Figure 12b show the areas that gave positive tests and arrow number 4 shows the area with a negative test by fluorescence quenching.)

Figures 13a and 13b are photographs taken in Building 852-3, a DNT "sweat house". These are respectively visible and ultraviolet photographs of the transite panel attached to the concrete wall just above a floor drain which is also pictured. In the prior test of this wall, solvent lifts tested negatively. However, in the UV photograph two distinct narrow dark lines can be seen in the lower left quadrant of the panel, indicating contamination. Another area on the concrete floor to the right and rear of the drain is also considered probably contaminated by reason of its lesser UV reflectance.

Figures 14a and 14b, again photographs with visible and ultraviolet reflectance, respectively, are of a portion of the floor in a tetryl packaging

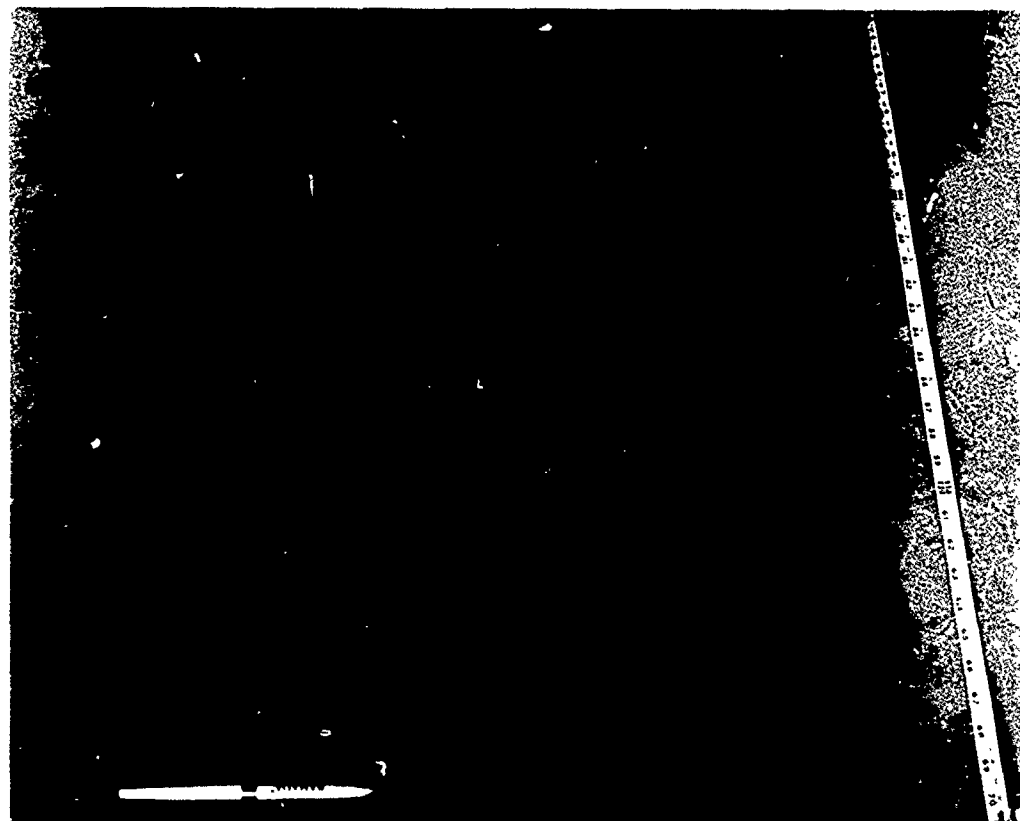


Figure 12. TNT Building E-4, Bay-1, JAAP  
 (a) (upper) visible reflection  
 (b) (lower) UV reflection

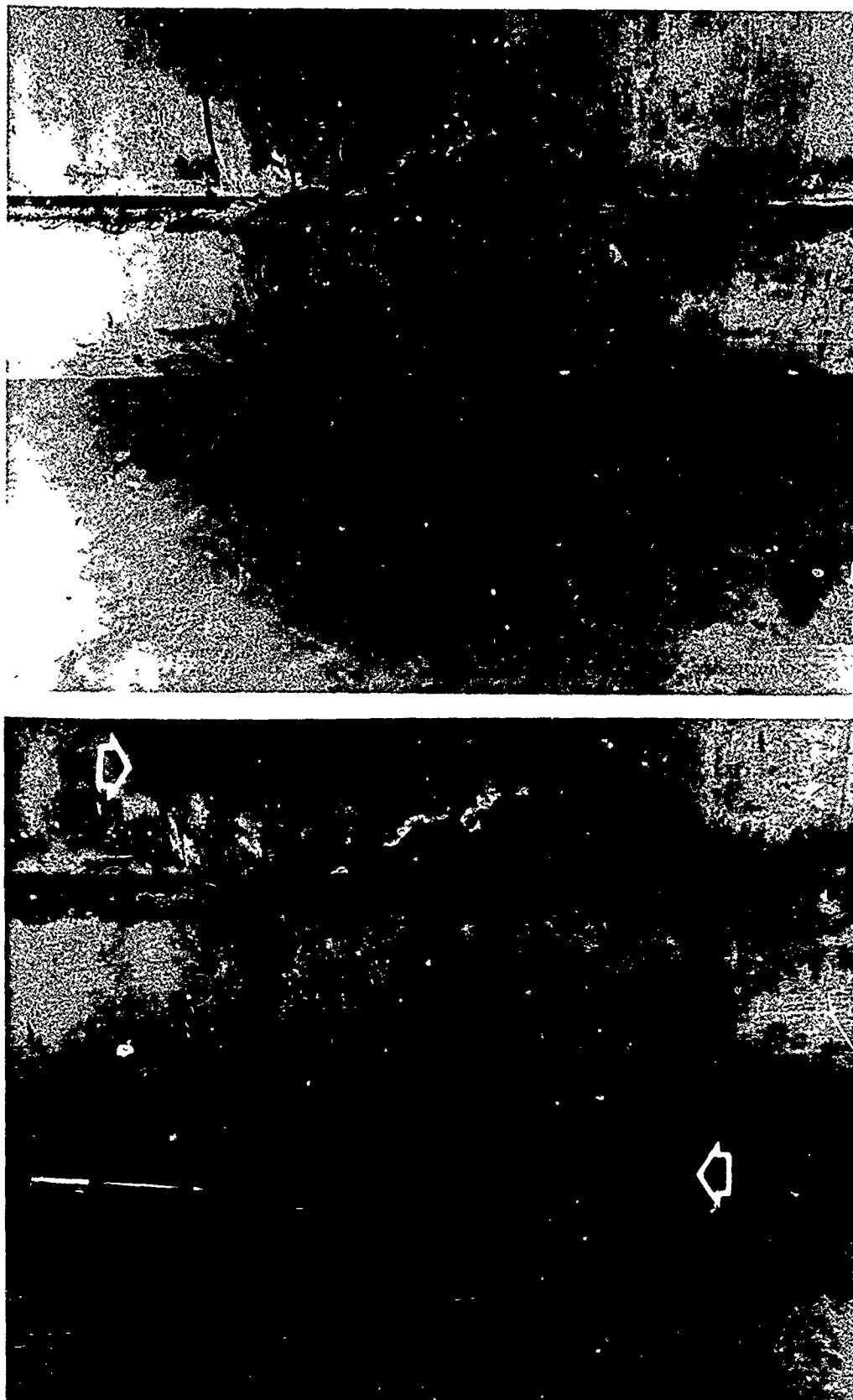


Figure 13. DNT Sweathouse, Building 852-3, JAAP

- (a) (upper) visible reflection
- (b) (lower) UV reflection



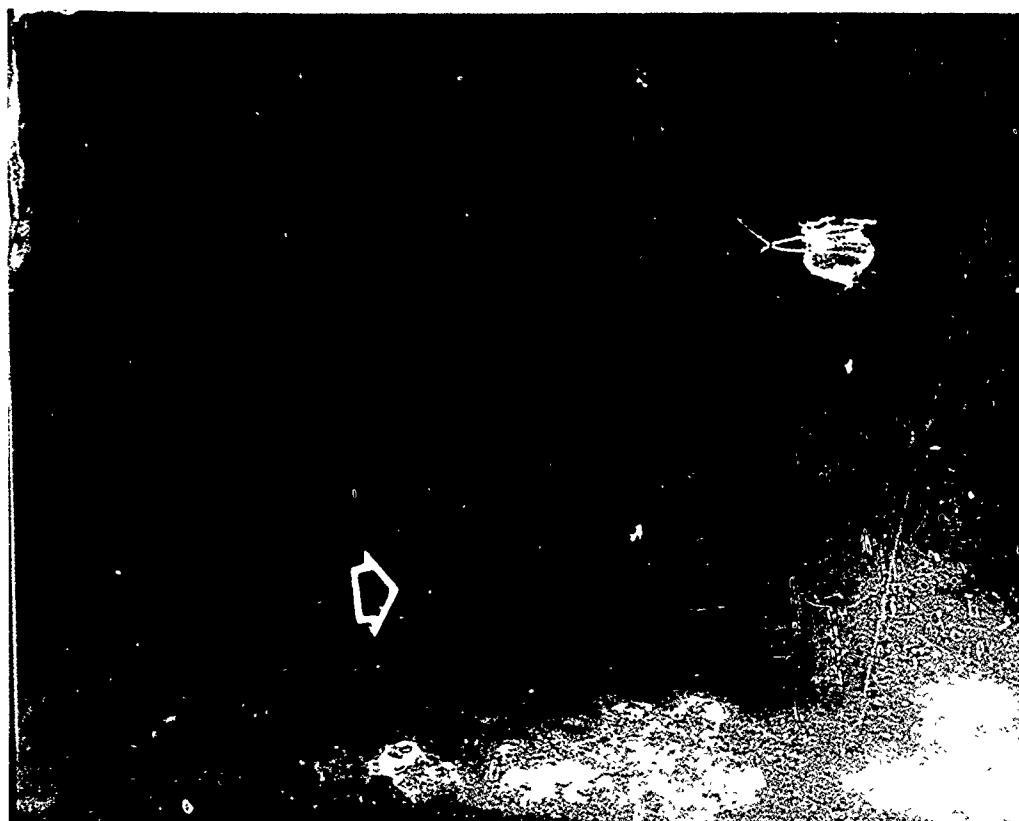
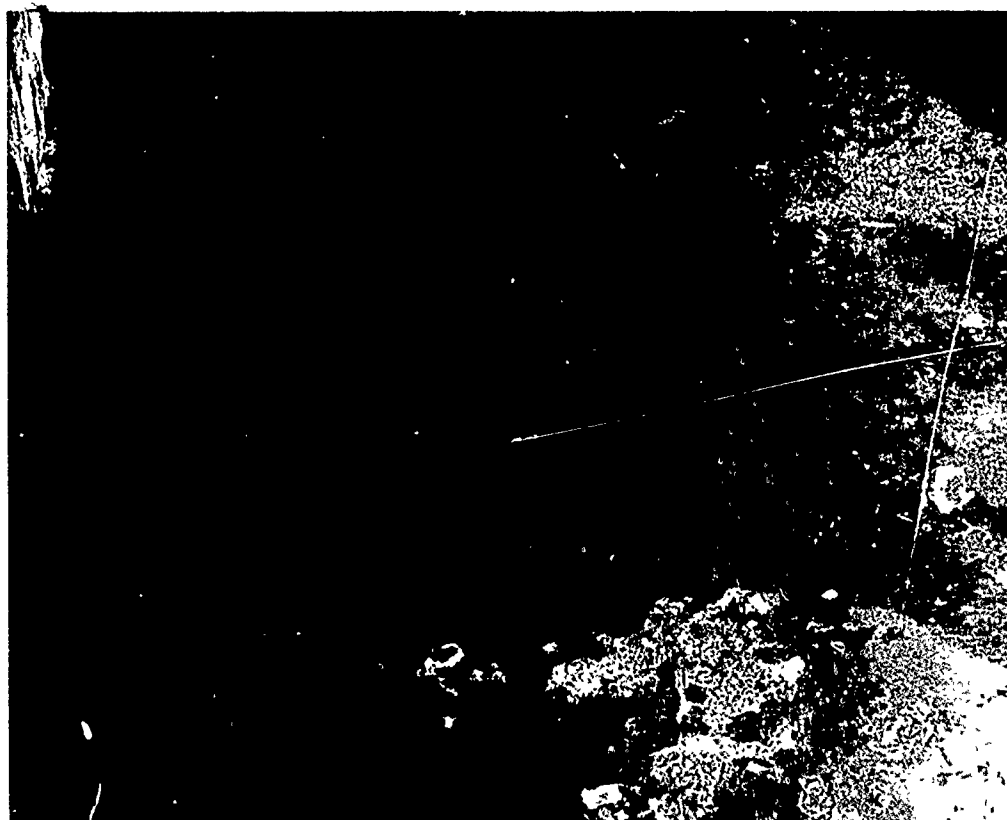


Figure 14. Tetryl Building, JAAP

- (a) (upper) visible reflection
- (b) (lower) UV reflection

building. The floor in this area is concrete to which a conductive coating had been applied. Any dark splotches that are seen in the UV photograph are considered suspicious even if apparent in the visible photograph. Teteryl is known to take on a strong yellow coloration on the test substrates and would be expected to show a different reflectance from background in both UV and visible light photography. (An arrow in Figure 14b indicates an area that is distinctly different from the overall background.)

In addition to the photography done with the 120 roll film at the Joliet AAP, a series of photographs were taken using Polaroid Type 667 positive print film, primarily as on-site documentation of the areas tested. Both visible and UV photography were utilized and upon later study, it became apparent that the differences in UV reflectances were as evident on the Polaroid as in the roll film system. The quality of the Polaroid film prints is not so good as those from the 120 negatives but is considered adequate for near real-time screening of surfaces for contamination. Preparation of additional prints and/or magnified prints would be less readily done with the Polaroid film than can be done with the 120 film.

### 2.3 Ultraviolet Video Camera Feasibility

In contrast to photographic methods, a UV video camera system would provide an instant image on the monitor and would allow a convenient and adaptable survey of suspicious surfaces. Although this mode of operation appears superior to still photography, there are important trade-offs to consider in the technical details of the two systems, not all of them in favor of video.

The convenience of video stems chiefly from its real-time operation compared to the more complicated cycle involved in photography: setting up, focusing, exposing, developing, and printing. However, the "instant" operation of the video camera would require a much larger illuminant power than a photographic camera would need. The vidicon in the TV camera needs an exposure (for every frame) not very different from the exposure needed on a film. While the photographic camera can, without any extra inconvenience, make up for a weak illuminant by long exposure, the video camera requires 30 exposures per second. The average power requirements for a video illuminator may, therefore, be two or three orders of magnitude larger than those needed for photography. In practical terms, this would mean a much heavier, bulkier, and expensive illuminator for video, requiring substantial AC line power.

### 2.3.1 Estimates of Performance and Illuminant Requirements

An equation to express the illuminant power required for video recording of an area is as follows:

$$P = 4EA_i f^2 \left(\frac{1+m}{m}\right)^2 (RTt)^{-1}$$

P = illuminant power (W)

t = exposure time (sec)

E = exposure (W sec/cm<sup>2</sup>)

A<sub>i</sub> = image area (cm<sup>2</sup>)

A<sub>o</sub> = object area (cm<sup>2</sup>)

f = f number of lens

m = magnification = A<sub>i</sub>/A<sub>o</sub>

R = diffuse reflectance

T = transmittance of the lens

Using a set of parameters listed below as an example, the illuminant power for a UV vidicon (Mod. N983, Hamamatsu) is: P = 15.9 watt. Parameters used in the calculation are as follows:

E = 3.3 x 10<sup>-8</sup> Wsec/cm<sup>2</sup> (from manufacturers specifications)

A<sub>i</sub> = 0.95 x 1.27 cm<sup>2</sup> (vidicon cathode size)

f = 8 (Zeiss UV-Sonnar lens; max. f-No. = 4.3)

R = 0.3 (diffuse reflectance of object area)

t = 1/30 sec

A<sub>o</sub> = 95 x 127 cm<sup>2</sup> (at 10 m distance with focal length 10.5 cm of the UV-Sonnar lens)

m = A<sub>i</sub>/A<sub>o</sub> = 10<sup>-4</sup>

T = 0.64 (at 254 nm, from manufacturers specifications)

Obviously, the required illuminant power is rather large; in terms of irradiance (P/A) it is about 5 times greater than that estimated for UV photography (cf. Section 2.2.2). The UV video camera has the advantages of providing a real time, continuous view of the UV scene, a convenient record of the entire operation on video tape with sound track, and individually

adjustable gain and contrast. The image resolution is poorer than with UV photography (line structure). Also, the video camera with recorder and monitor are heavier and more expensive than the photographic camera.

### 2.3.2 Video Camera with Frame Subtraction Processor and Synchronized Illuminator

In addition to the conventional use of the UV video camera, a concept was developed for a method of utilizing the capabilities of the video system to improve the discrimination of the significant features of the image and to reject irrelevant features resulting from the surface pattern of the object and accidental glints. Since such features would appear both in the visible and in the UV, a great improvement in the detection of UV features could be obtained by subtracting the visible image from the UV image. The "difference image" would then show only those features that have a spectral contrast.

The only illumination system considered in this analysis of the video camera system feasibility was the use of flash tubes. Although some other types of UV sources might meet the illuminant power requirements, only the flash tube approach is capable of generating the type of data required for the "difference image" signal processing. The "difference image" approach was, in turn, considered the most attractive procedure for generating useful information from the video camera in real time, especially in view of its limitations on resolution. The pulsed nature of the information generated by the flash lamps allows direct subtraction of one image from another after digitization; this would be difficult or impossible if continuous illumination sources were used.

A block diagram (Figure 15) shows a suggested approach to generate UV minus visible difference images in real time on a video system. It works as follows: flash tubes are alternately operated in synchronism with the TV camera. The first frame is exposed with UV and visible light from a quartz envelope flash tube type FX 193U (EG&G). The video from this frame is digitized and stored in a frame memory. The next frame is exposed with visible light only from a glass envelope flash tube type FX 193. The video from that frame is digitized and doubled in amplitude and then subtracted in the frame memory from the previous frame. The result is:

$$UV + VIS - 2VIS = UV - VIS$$

The "difference image" is now in the frame memory to be displayed on the monitor. The result is a spectral difference image in real time. Note that this scheme is made possible by the availability of the flash tube FX 193 with two optional types of envelopes. The quartz envelope (Model 193 U) transmits both the visible and UV radiation while the glass envelope (Model 193) transmits only the visible radiation.

The reason for this approach to image subtraction is that short wave UV transmitting, visible blocking filters are typically very inefficient. The

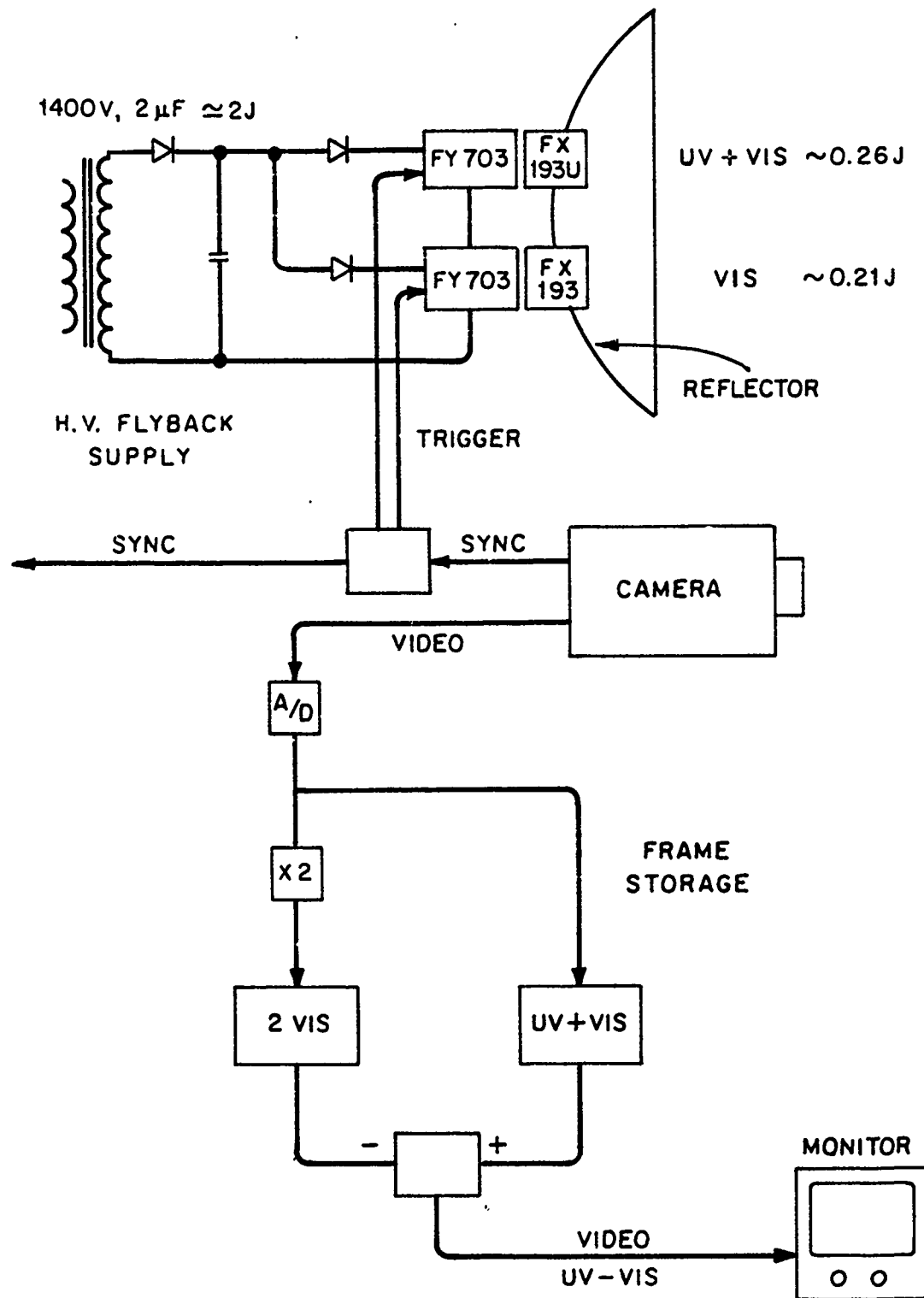


Figure 15. Block Diagram of UV Video Concept

proposed method uses instead the UV absorption in the flash tube envelope to provide spectral discrimination. The intensity of the visible flash (from FX 193) would have to be made separately adjustable by the operator in order to control the degree of visible image cancellation. Alternatively, separate video gain controls for subsequent frames could be used.

This proposed method would have the general advantages of the UV video system plus the enhanced discrimination of the UV spectral features. It is, however, only in the conceptual stage and would require development of the processing software and illuminator hardware before possible implementation. The overall summary of the feasibility of the UV video system is:

- Use of a video camera in the contemplated surface sampling protocol is feasible. A video camera would permit real-time scanning of surfaces.
- Use of a video camera system having image processing capability would permit enhancement of the contrast between clean and contaminated surfaces. An approach to designing a system having this capability has been proposed as part of this study. This capability is considered the principal advantage of using a video camera system.
- The advantages of video camera use are obtained at the expense of larger average illuminant power requirements. These requirements would have to be satisfied by using a more powerful UV illumination source with its attendant undesirable characteristics such as cost, weight, and power requirements, or by settling for a greatly reduced viewing area.

#### 2.4 Thermal Imaging

The potential for thermal imaging radiometry to detect explosives on building material surfaces depends on the absorption of UV radiation by the explosive with a resultant increase in infrared (IR) emission in the 8 to 14  $\mu\text{m}$  wavelength area. Thermal imaging systems exist that can detect the IR radiation and convert it to a video or photographic presentation. The commercially-available instruments cover the 8 to 12  $\mu\text{m}$  window within the overall 8 to 14  $\mu\text{m}$  IR emission region. The approach during this program was to illuminate the analyte/surface combinations with the same illuminator (cf. Section 2.2.2) as for the UV photography and to determine any resultant temperature differential with a video type thermal imaging radiometer (Model 525L, Inframetrics, Bedford, Mass.). The same analyte/surface combinations used in the evaluation of the UV photographic system (cf. Section 2.2.3) were investigated by thermal imaging radiometry. Experimental thermal imaging radiometry was carried out simultaneously with photographic studies during the laboratory studies and the results were observed both immediately on the system's video monitor and subsequently on the scenes as recorded on video tape.

To reiterate the conditions of UV photography, the amounts of each analyte applied to 10 cm<sup>2</sup> on each substrate ranged up to maximums of 5 mg each on brick, 2.5 mg on wood and 2 mg on concrete, transite, and stainless steel. Even at such high concentrations, the thermal imaging radiometry did not show any distinction of the analytes from the substrates whether as monitored directly or when the video tapes were studied afterwards.

The reasons for the lack of detection of all of the analytes on any of the surfaces are probably related to two properties of the substrates combined with the illumination system, namely UV absorption at 254 nm and emission or reflection of IR in the 8-12  $\mu$ m band. As was seen from Figures 1 and 2, the substrates do absorb UV radiation and thermal emittance is then a good possibility. Additionally, during observations while conducting the thermal imaging experiments, it was determined that the illuminator itself was delivering a large amount of radiation in the 8-12  $\mu$ m band to the analytes and surfaces. This radiation then contributed to some temperature increase for both analyte and background.

Since the UV and thermal radiations from the germicidal lamp arrangement contributed simultaneously to the insensitivity of the thermal detection system, an experimental approach was made to elucidate the UV effect. In these experiments, the high pressure mercury lamp evaluated in Section 2.2.2 (Osram high pressure mercury lamp) was chosen as an intense source of 254 nm UV. This lamp and its configuration allowed for total filtration of any IR radiation in the 8-12  $\mu$ m range; the filtration was accomplished with the use of a<sub>3</sub> continuously cooled solution containing nickel sulfate and cobalt sulfate. The Osram lamp produced an irradiated oval area approximately 3 x 5 cm in size. A peak irradiance of 30 mW/cm<sup>2</sup> was measured with the previously described Model 1L 700-A Radiometer with a Model SEE-240 Detector (cf. Table 1, Section 2.2.2).

2,4-DNT was selected as a model analyte in this study since it's UV absorbance at 254 nm was among the highest of the analytes of interest (cf. Figure 1, Section 2.1). Concrete and brick were used as test surfaces because they represented a medium and a low reflectance substrate. The 2,4-DNT was applied in 500  $\mu$ g quantities to 10 cm<sup>2</sup> circles on each of the substrates. The 2,4-DNT was a solution in acetonitrile prepared from a bulk sample of the analyte.

The Inframetrics thermal radiometer was operated in the line scan mode, in the 10°C range, with level compensation, the readings of which were used to calculate the temperatures. IR emissivity was taken as 0.93 for both the brick and cement surfaces.

In order to be sure the steady-state temperature was attained, each area was irradiated for 10 minutes. After such time the temperature rises caused by UV irradiation (at 30 mW/cm<sup>2</sup>) were between 1.4 and 2.7°C, as shown below.

DNT on brick	2.3°
Uncoated brick	2.7°
DNT on cement block	1.4°
Uncoated cement block	1.8°

In both cases the temperature of the uncoated substrate was higher than that with the analyte applied, contrary to expectation. This could be caused either by the substrate having absorptance greater than the analyte, or the analyte increasing the reflectance of the coated substrate. Either way, the difference ( $\sim 0.4^{\circ}\text{C}$ ) is rather small and barely useful for detection purposes in view of the limited temperature resolution of the instrument ( $\pm 0.2^{\circ}\text{C}$ ). In view of the discouraging outcome of this and the prior tests of all analytes on all surfaces, the IR thermal method was abandoned, and the experimental program was concentrated on the UV photographic detection method as described above.



### 3. CONCLUSIONS

Laboratory experiments showed conclusively that most of the analytes of interest can be detected photographically by reflected ultraviolet radiation when these analytes are on stainless steel, concrete, and transite. With SARM materials, TNT and tetryl were detected in 10 cm<sup>2</sup> areas of those surfaces at concentrations of 10 µg/cm<sup>2</sup> and 2,4-DNT, 2,6-DNT, RDX and DPA were detected at 20 µg/cm<sup>2</sup> levels. With bulk samples of the analytes, the corresponding concentrations of these materials were decidedly higher. Bulk TNT, tetryl and RDX were detected at levels of 25 µg/cm<sup>2</sup>. 2,4-DNT, 2,6-DNT, and DPA were detected at 50 µg/cm<sup>2</sup> on concrete and at 25 µg/cm<sup>2</sup> on transite and stainless steel. PETN from the bulk sample could only be detected at 100 µg/cm<sup>2</sup> on concrete and transite and at 150 µg/cm<sup>2</sup> on stainless steel. At levels up to 250 µg/cm<sup>2</sup> on wood and 500 µg/cm<sup>2</sup> on brick, none of the analytes could be detected by UV photography. It appears that at 254 nm, wood and brick have the same order of UV reflectance as the analytes themselves.

A battery of four germicidal lamps was designed to deliver the required illumination of analytes on the materials which were then photographed. The 254 nm reflection differences were best discriminated with the use of a narrow band pass interference filter (Corion Corporation) used with a Zeiss UV transmitting lens mounted on a Hasselblad camera body. Kodak Tri-X and Polaroid Type 667 films were found useful for recording the reflectance differences. The Polaroid film presents the same pictorial data as the Tri-X but does not allow adequate reproduction or enlargement.

UV photography was carried out at selected areas of both the Holston AAP and Joliet AAP. The photography at the former site showed no definite areas of contamination and probable evidence on one tool (a skimmer). It is to be noted that prior chemical tests in the general areas of this site also showed negative results. It was at this site, where a Schott UG-5 filter was used, that the discovery was made that any radiation from 650 nm to the near-IR region was effective in exposure of the film. This led to the final selection of the Corion filter.

Several areas photographed at the Joliet AAP, using the Corion filter, showed distinctive differences in reflections of the 254 nm illumination. One area was simultaneously tested chemically and positive and negative results of both methods were in agreement. Because of time constraints other areas photographed could not be screened by the chemical tests (i.e., the solvent-wick test as detailed in an earlier project<sup>2</sup>).

The concept of using a video system for ultraviolet reflection was evaluated using available information and calculations for such devices. The concept does appear feasible for surveillance of large areas in real-time, although source power limitations might make a video system less practical than photography.

The use of ultraviolet-stimulated thermal imaging methodology to detect small temperature differences of analytes on the substrates was not successful in locating the analytes. From the data obtained, it is concluded that discrimination of analytes from substrates is not feasible by this method without considerably increasing the sophistication of the system.

#### 4. RECOMMENDATIONS

The field evaluation tests done during this project were primarily to demonstrate the capability of UV photography to examine larger areas in shorter times than had been possible with earlier surface testing. From the results of the photography at the Joliet AAP, it is apparent that concrete, transite, and one example of conductive flooring showed areas of diminished UV reflectance compared to surrounding or adjacent areas. In one such area, confirmatory tests were made with solvent-wick extractions of material onto filter paper. These extracts, after drying, were tested for the quenching of anthracene fluorescence and the positive results were in agreement with the lesser UV reflection. It is recommended that a further evaluation of field sites be made combining confirmatory tests with UV photography to establish the validity of the UV detection method. Such an evaluation would necessarily involve a much greater labor effort than was budgeted during this just completed project. It is anticipated that the principal advantage of the UV photography system will be to differentiate, in a rapid survey mode, potentially contaminated areas from those showing no evidence of contamination. Then, only the potentially contaminated areas would need to be examined by a confirmatory technique such as the solvent-wick test.

Consideration should be given to a methodology combining solvent-wicking and UV photography so that any contamination would be transferred to a highly reflective substance and be detected. Such a methodology might allow photographic detection of materials on wood and brick.

A more flexible illumination system should be designed so all surfaces can be evenly illuminated. This might be accomplished with a more portable system including a swivel mechanism for the ultraviolet lamp frame.

Polaroid film of the positive/negative types should be investigated for detection of the analytes so that subsequent enlargements could be made and examined. However, use of such film requires a source of fresh (running) water for prompt rinsing of the negatives. A portable wash/preserving system could be designed for treatment of the negatives during field tests in sites where running water is not available.

The use of a "flying spot" illuminating system for high UV intensity at greater operating distances should be investigated. Such a device would allow larger areas to be examined both photographically and by a video system than were possible with the illuminator used for this project. The "flying spot" system would involve focussing a UV source (perhaps a laser) to increase greatly the illumination on a small area. This spot of UV illumination would be swept across the area to be surveyed in the manner of a line scan for video purposes. A synchronously moving rapid detection system would move with the spot or a large aperture detector could register the local effects.

The feasibility of video monitoring UV reflections should be evaluated experimentally to determine whether a real time examination system will work. For any reflection system, image subtraction techniques using two wavelengths should be evaluated for enhancement of the information detected.

#### REFERENCES

1. Patterson, J., et al., In Vol. I of State-of-the-Art: Military Explosives and Propellants Production Industry (3 Vols.), EPA-600/2-76-213a, October 1976, p. 38.
2. Goodwin, B., et al., Surface Sampling Techniques. Report No. DRXTH-TE-CR-82179, September 1982; Defense Technical Information Service No. A120857.
3. L.R. Koller, Ultraviolet Radiation, John Wiley & Sons, New York, 1952, pp. 161-163.

APPENDIX I

## SURFACE SAMPLING TECHNIQUES: PROPOSED SAMPLING PROTOCOLS

Introduction. Under Contract No. DAAK 11-83-R-0042 to USATHAMA, Arthur D. Little, Inc. is performing research and development work on surface sampling techniques. The objective of this work is the development and field testing of prototypes for UV photography and thermal imaging methods for detection of explosives and explosives by-products or common building material surfaces. Our program to accomplish that objective includes laboratory experiments to be performed over a 4-5 month period starting during the current reporting period (November 1983) and extending through March-April 1984. During that time, we plan to perform at least three types of experiments, namely:

- Preliminary experiments in which we shall determine the UV reflectance properties of each of the surface types and analytes of interest and of analyte-surface combinations. This work will aid in the selection of an ultraviolet illumination source for the prototype systems;
- Developmental experiments intended to optimize system configurations for each analyte-surface combination with the objective of obtaining the lowest possible detection limit; and,
- Qualitative certification experiments to validate the methods that are developed. These experiments will be conducted in accordance with the requirements of the April 1982 USATHAMA QA Plan.

All of these experiments will involve the investigation of samples of each of the surface types and analytes listed in Table 1. Most of these experiments will involve, in turn, the examination of samples prepared

Table 1

### Surface Types and Analytes to be Investigated

#### Surface Types:

Concrete - unpainted  
Brick - glazed  
      - unglazed  
Transite  
Wood  
Metal

#### Analytes:

2,4,6-TNT  
2,6-DNT  
2,6-DNT  
RDX  
PETN  
Tetryl  
DPA

by applying known amounts of analytes to previously clean, uncontaminated samples of the various surface types. The purpose of this report is to describe the methods we propose to use for the procurement of samples of surfaces and analytes and for preparing samples for examination.

Procurement of Samples. For surface samples, we propose to use new, unused building materials purchased from local building materials supplies dealers. For selection of specific items representative of each of the surface types of interest we shall use the following criteria:

- The item should be readily available in unlimited supply; and,
- It should be representative of the types of materials actually used in AAP construction and operation.

Examples of the types of materials which satisfy these criteria are listed in Table 2.

Table 2

Building Materials Representative of Surface Types of Interest

<u>Surface Type</u>	<u>Building Material</u>
Concrete - unpainted	Concrete patio block, 2" thick
Brick - glazed	Glazed drain tile
- unglazed	Common red brick with <u>no</u> color or texture added
Transite	Asbestos millboard, 1/4 - 3/8" thick
Wood	Western fir/spruce kiln-dried premium grade dimension lumber
Metal	Stainless steel plate

In every case we shall select only items which appear to be clean and free from any dust, dirt, or other extraneous material.

For analyte samples, we plan to use materials supplied by USATHAMA. It is desirable to minimize the occurrence of false positive or false negative responses which could result from the presence of impurities in analyte samples. To this end, it would seem to be advisable to use SARM materials as analyte samples in all experiments. We recognize, however, that the Army seeks to limit the use of SARMS to circumstances



requiring high-purity standard reference materials. A grade of material other than SARM may be acceptable for the planned preliminary and developmental experiments, provided that sufficient SARM material can be made available for comparison purposes if the possible presence of interfering impurities in the non-SARM materials becomes an issue. For qualitative certification experiments, we plan to use only SARM material. Estimates of the required quantities of SARM and non-SARM materials are given below.

Preparing Samples for Examination. Metal and glazed brick samples will be washed with acetone and dried thoroughly before use to remove any adhering film of oil, grease, etc. All other surface samples will be used without prior treatment of the surface to be examined.

We plan to apply analytes to surfaces as solutions, using the same procedures that were employed successfully in our previous work for USATHAMA on surface sampling techniques under Contract No. DAAK11-81-C-0014. The advantage of this approach include the following:

- It permits accurate, precise manipulation of small quantities of analyte while minimizing opportunities for analyte loss or contamination.
- It provides probably the most reasonable approximation of the processes responsible for contamination of surfaces during AAP operation.
- Penetration of analyte into surface samples can be controlled by selection of organic solvents having particular surface wetting characteristics and volatility

Stock solutions of each analyte will be prepared by adding weighed amounts of analyte to a reagent grade solvent such as acetonitrile and diluting to a predetermined volume. The resulting solutions will be stored in the glass-stoppered volumetric glassware in which they were prepared, under ambient conditions and out of direct sunlight. Analyte concentrations in stock solutions will typically be 0.1% (w/w) or greater.

Working solutions will be prepared fresh daily from stock solutions by volumetric dilution. Desired volumes of working solutions will be applied directly to surfaces using volumetric pipets (for volumes  $\geq 1$  mL) or adjustable autopipets (for smaller volumes). The actual volume of solution delivered by each autopipet used will be checked periodically by weighing a nominal delivered volume and calculating the actual delivered volume using the reported density of the solvent. The area over which the solvent spreads will be checked immediately after application and then the solvent will be allowed to evaporate under ambient conditions prior to any further manipulation of the sample.

Quantities of Analyte Samples Required. Because of the nature of this research and development work, the exact experiments and thus the total quantities of analyte samples which we may require cannot be specified exactly. The following rough estimates are provided for guidance in determining the quantities of SARM and non-SARM analytes may be required for the various types of planned experiments.

Preliminary Experiments. In these experiments we plan to determine the diffuse reflectance of each of the surface types and analytes of interest and of analyte-surface combinations using a UV-visible spectrophotometer equipped with an integrating sphere. To determine the reflectance properties of the analyte neat and on a surface, we plan to examine a sufficient quantity of material in each case to assure that we are "seeing" the analyte. For this purpose, we may assume that it will be sufficient to examine 5 cm<sup>2</sup> of analyte 0.5 mm in thickness. The quantities of each analyte corresponding to this equivalent volume are shown in Table 3.

Table 3

Quantities of Analytes Required for Determination  
of Diffuse UV Reflectance

<u>Analyte</u>	<u>Density, g/cm<sup>3</sup> (Handbook of Chem. and Physics)</u>	<u>Grams of Analyte in 0.25 cm<sup>3</sup> Volume</u>	<u>X7 Expts = Total Quantity Required</u>
TNT	1.654	0.41	2.9
2,4-DNT	1.321	0.33	2.3
2,6-DNT	1.2833	0.32	2.2
RDX	1.82	0.46	3.2
PETN	1.773	0.44	3.1
Tetryl	1.57	0.39	2.7
DPA	1.160	0.29	2.0

Systematic investigation of each analyte neat and applied to each of the 6 surface types would require a total quantity of each analyte equal to seven times the amount indicated in the third column of Table 3. The resulting quantities of each analyte as shown in the last column of Table 3 range from 2.0 DPA to 3.2 g RDX

Developmental Experiments. These experiments, to be performed during the December 1983 - March 1984 reporting periods, will have the following objectives:

- Determination of the detection limit of both the UV photography and thermal imaging protocols. This information is essential to designing subsequent experiments directed

toward improving the image contrast obtainable with both protocols. These experiments are separate from the qualitative certification planned later in the program for the prototype methods recommended for field testing.

- Determination of Optimum Equipment Configurations for Each Analyte-Surface Combination. Factors to be addressed in these experiments include, in addition to detection limit, viewing area, ease of handling and operation, personnel safety, and analysis time.

All of these experiments will involve examination of surface samples to which known quantities of analytes have been applied using the procedures described in the preceding section. Analytes will be applied to 10 cm<sup>2</sup> areas of approximately circular dimensions on each surface type. The selection of a 10 cm<sup>2</sup> application area is largely arbitrary but is intended to provide sufficient "contaminated" area for viewing together with clean "uncontaminated" surface while minimizing the amount of analyte used. The volume of analyte working solution delivered to the surface at one time will be just sufficient to cover 10 cm<sup>2</sup>; the amount of analyte delivered in that volume will be varied by using working solutions of different concentrations. To minimize the opportunities for sample contamination and analyte degradation or loss, samples will be prepared fresh daily.

Determination of detection limits will require preparation of surfaces to which varying quantities of analytes have been applied. For illustrative purposes, we may assume that it will be sufficient to examine 5 different analyte concentrations ranging from 100 to 1000 µg/cm<sup>2</sup>, and that up to 4 experiments each requiring one day may be required. The total amount of analyte required may then be calculated as shown in Table 4.

For determination of optimum equipment configurations, we may again assume for illustrative purposes that experiments involving 2 different analyte concentrations at the lower end of the range examined previously will be performed on each of a total of 60 days. The total amount of analyte required may then be calculated as follows:

$$\begin{aligned}
 & 1 \text{ analyte} \times 6 \text{ surface types} \times \begin{cases} 250 \text{ } \mu\text{g}/\text{cm}^2 \\ 100 \text{ } \mu\text{g}/\text{cm}^2 \end{cases} \times 10 \text{ cm}^2 \times 60 \text{ days} \\
 & = \begin{cases} 900 \text{ mg} \\ 360 \text{ mg} \end{cases} \\
 & \text{Total } 1260 \text{ mg of each analyte}
 \end{aligned}$$

Table 4

Quantities of Analytes Required in Developmental  
Experiments for Determination of Detection Limits

<u>Analyte Concn.</u>	<u>Area</u>	<u>Quantity Of Analyte</u>
1000 $\mu\text{g}/\text{cm}^2$	10 $\text{cm}^2$	10 mg
750 "	"	7.5 mg
500 "	"	5 mg
250 "	"	2.5 mg
100 "	"	1 mg
Subtotal		26 mg
x 4 experiments		104 mg
x 6 surface types		
Total		624 mg of each analyte

This amount combined with the quantity of analyte calculated in Table 4 gives the total amount of analyte required for developmental experiments:

$$624 \text{ mg} + 1260 \text{ mg} = 1884 \text{ mg} \approx 1.9\text{g of each analyte.}$$

Qualitative Certification. The protocols developed in the preceding experiments will be validated using the qualitative certification procedures described on pp. 22-24 of the April 1982 USATHAMA QA plan. Assuming that we prepare for this purpose four standard spiked samples of each analyte on each surface and that the detection limit will be  $\approx 250 \mu\text{g}/\text{cm}^2$ , the total amount of analyte required for qualitative certification may be calculated as follows:

$$1 \text{ analyte} \times 250 \mu\text{g}/\text{cm}^2 \times 10 \text{ cm}^2 \times 4 \text{ standard} \times 6 \text{ surface} \\ \text{spiked} \quad \text{types} \\ \text{samples}$$

$$= 60 \text{ mg of each analyte}$$

Total Quantities of Analyte Samples Required. The preceding estimates of SARM and non-SARM analytes required for each type of experiments is summarized in Table 5.

Table 5

Total Quantities of Analyte Samples Required

<u>Type of Experiment</u>	<u>Type of Material</u>	<u>Total Amount of Each Analyte Required</u>
Preliminary	Non-SARM	2.0-3.2 g (see Table 3)
Developmental	Non-SARM	1.9 g
Qualitative Certification	SARM	60 mg
Total		$\approx 4.0 - 5.2 \text{ g}$

APPENDIX II

## SURFACE SAMPLING TECHNIQUES: PROPOSED ANALYTICAL METHODS

Introduction. Under Contract No. DAAK 11-83-R-0042 to USATHAMA, Arthur D. Little, Inc. is performing research and development work on surface sampling techniques. The objective of this work is the development and field testing of prototypes for UV photography and thermal imaging methods for detection of explosives and explosives by-products on common building material surfaces. Our program to accomplish that objective includes laboratory experiments to be performed over a 4-5 month period starting during November 1983 and extending through March-April 1984. During that time, we plan to perform at least three types of experiments, namely:

- Preliminary experiments in which we shall determine the UV reflectance properties of each of the surface types and analytes of interest and of analyte-surface combinations. This work will aid in the selection of an ultraviolet illumination source for the prototype systems;
- Developmental experiments intended to optimize system configurations for each analyte-surface combination with the objective of obtaining the lowest possible detection limit; and
- Qualitative certification experiments to validate the methods that are developed. These experiments will be conducted in accordance with the requirements of the April 1982 USATHAMA QA Plan.

All of these experiments will involve the investigation of samples of each of the surface types and analytes listed in Table 1. Most of these experiments will involve, in turn, the examination of samples prepared

Table 1

### Surface Types and Analytes to be Investigated

#### Surface Types:

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Metal

#### Analytes:

2,4,6-TNT  
2,4-DNT  
2,6-DNT  
RDX  
PETN  
Tetryl  
DPA

by applying known amounts of analytes to previously clean, uncontaminated samples of the various surface types. Detailed descriptions of the sampling protocols we propose to use are given in the Proposed Sampling Protocols Technical Report submitted previously. The purpose of this report is to describe the analytical methods we propose to use for the examination of samples.

Preliminary Experiments. In these experiments we plan to determine the diffuse reflectance of each of the surface types and analytes of interest and of analyte-surface combinations using a Beckman DK-1A UV-visible spectrophotometer equipped with an integrating sphere. To determine the reflectance properties of the analyte neat and on a surface, we plan to examine a sufficient quantity of material in each case to assure that we are "seeing" the analyte. For this purpose, we may assume that it will be sufficient to examine 5 cm<sup>2</sup> of analyte 0.5 mm in thickness. To maintain the sample in the proper position during analysis may require the use of double-sided adhesive tape or similar aids. In such cases additional experiments will be run to determine the contribution, if any, of the tape or equivalent to the observed spectra.

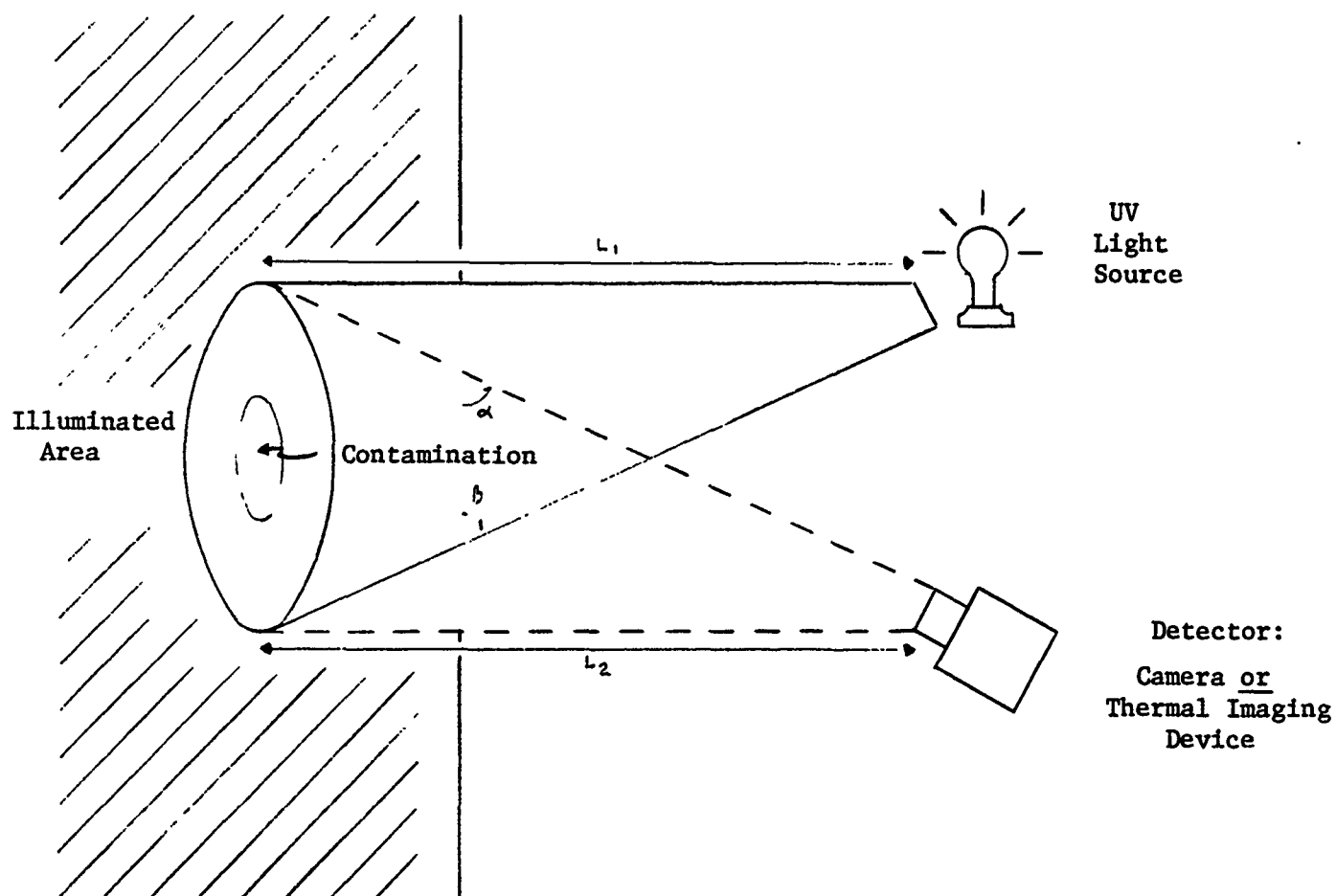
Developmental Experiments. These experiments, to be performed beginning when we have received the quantities of SARM and non-SARM reference materials specified in the Proposed Sampling Protocols Technical Report and extending through March 1984 reporting periods, will have the following objectives:

- Determination of the detection limit of both the UV photography and thermal imaging protocols. This information is essential to designing subsequent experiments directed toward improving the image contrast obtainable with both protocols. These experiments are separate from the qualitative certification planned later in the program for the prototype methods recommended for field testing.
- Determination of optimum equipment configurations for each analyte-surface combination. Factors to be addressed in these experiments include, in addition to detection limit, viewing area, ease of handling and operation, personnel safety, and analysis time.

The analytical methods we propose to use for these experiments are represented schematically in Figure 1. The UV illumination source selected upon completion of the Preliminary Experiments will be used in all Developmental Experiments to illuminate the surface under examination. For the UV photography sampling protocol the Hasselblad Model 500 C/M camera and Zeiss UV Sonnar lens will be used as the detector. For the thermal imaging sampling protocol an Inframetrics Model 525 TV compatible Imaging Radiometer will be used as the detector. The thermal imaging system will be equipped with an IR/VIS filter developed under a separate subtask under this contract subsequent to selection of a specific UV illumination source.



UV PHOTOGRAPHY/THERMAL IMAGING SAMPLING PROTOCOL



PROCEDURE

1. Illuminate surface with UV light
2. View illuminated area with camera or thermal imaging device

Figure 1

In the developmental experiments we shall systematically vary the distance of the UV illumination source from the surface under examination ( $L_1$  in Fig. 1), the distance of the detector from the surface ( $L_2$  in Fig. 1), and the angles of illumination and viewing ( $\alpha$  and  $\beta$ , respectively, in Fig. 1) in order to obtain the optimum contrast between the contaminated area and surrounding surface in the images obtained by both analytical methods. Additional specific instructions for instrument calibration, use, and maintenance will be developed as our work proceeds.

Qualitative Certification. The protocols in the preceding experiments will be validated using the qualitative certification procedures described on pp. 22-24 of the April 1982 USATHAMA QA Plan.

APPENDIX III

## SOLVENT-WICK METHOD FOR EXPLOXIVES ON SURFACES

Reference: Goodwin, B., et al., Surface Sampling Techniques, Vol. I. Report DRXTH-TE-CR-82179, September 1982; Defense Technical Information Service No. A120857.

Sampling: 1) Whatman No. 42 9.0-cm filter paper circles are saturated with 0.5-10.0 mL of acetonitrile; 2) the wetted paper is pressed against the surface of interest; 3) the filter paper is allowed to remain in place until the solvent has evaporated; 4) the filter paper is removed and stored in a 100 x 15 mm disposable plastic Petri dish until analyzed.

Analysis: 1) A cotton swab is used to apply a 100 µg/mL solution of anthracene in acetonitrile to the side of the filter that was in contact with the surface of interest; 2) the filter paper is visually examined under a UV lamp; 3) explosives residues at a level of 0.5 µg/cm<sup>2</sup> or higher are identifiable as dark areas where the anthracene fluorescence is quenched.

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